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THE MECHANISM OF THERMOLYSIS OF AN AZOALKANE

BY



PETER MURRAY POPE

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

AND RESEARCH

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EDMONTON, ALBERTA

FALL, 1971

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES
AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled THE MECHANISM OF THERMOLYSIS OF AN AZOALKANE submitted by Peter Murray Pope, in partial fulfilment of the requirements for the degree of Master of Science.

Date Fall 1971

TO MY PARENTS

A B S T R A C T

The azoalkane 1,1-diphenyl-1'-ethyl-1'-methylazo-methane, 4, was synthesized by three different routes. Optically active samples of 4 with known absolute configuration were prepared from (S)-(+)-2-butylamine. The absolute configuration and maximum rotation of the corresponding unsymmetrical coupling product 1,1-diphenyl-2-methylbutane, 14, were determined by synthesizing the optically active hydrocarbon from R-(-)-2-methylbutanoic acid.

The decomposition of optically active S-(-)-4 at 100° in benzene solution and in benzene solution 1 M in butanethiol yielded the hydrocarbon R-(-)-14 with 2% and 6% net inversion of configuration, respectively.

An estimate of the cage effect in the decomposition of 4 was made by product analysis. In benzene solvent the values obtained were approximately 10% both at 80° and 100° and in 1 M butanethiol in benzene solution the values were approximately 20% at these temperatures.

The kinetics for the decomposition of 4 were measured in a variety of solvents under different conditions. The decomposition rate of 4 decreased upon changing the solvent from octane to the more viscous alkane solvent hexadecane. The values obtained for the activation parameters for the decomposition of 4 in cumene solution were $E_a = 31.2 \pm 1.3$ kcal/mole, $\Delta H^\ddagger = 30.5 \pm 1.3$ kcal/mole and $\Delta S^\ddagger = 8.1 \pm 4.0$ e.u.

There is sufficient evidence to conclude that the decomposition of 4 proceeds by initial one-bond cleavage to produce the diphenylmethyl and 2-butylazo radicals. The effect of solvent viscosity upon decomposition rate implies that cage return of the radical pair occurs. During the decomposition of 4, the chemically induced dynamic nuclear polarization effect could be observed by nuclear magnetic resonance spectroscopy for the products but not for the starting material. This indicates that the 2-butylazo radical undergoes β -scission before it has a chance to diffuse from the solvent cage and reform 4 by coupling with a diphenylmethyl radical from another solvent cage.

A C K N O W L E D G E M E N T S

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I N T R O D U C T I O N

This investigation was undertaken as part of a research programme aimed at studying the stereochemistry of the cage combination of free radicals as well as mechanistic aspects of the thermal decomposition of azo compounds. Previous work pertaining to the stereochemistry of the making and breaking of bonds to an asymmetric carbon atom in free radical reactions has been extensively reviewed by Gillan (1) and Mojelsky (2).

The mechanism of the thermal decomposition of azo compounds has been investigated by many workers. Most work has been directed towards differentiating between a one and a two-step process. Ramsperger (3) studied the vapour phase thermal decomposition of azomethane, azo-bis-isopropane and methylazoisopropane. Because the activation energy of the thermolysis of the last compound was intermediate between those of the other two compounds, he suggested that there is concerted cleavage of both carbon-nitrogen bonds.

Cohen and Wang (4) measured the decomposition kinetics of azo-bis-diphenylmethane in toluene solution and compared the results with previously published data on the decomposition of azomethane, azo-bis-isopropane and azo-bis- α -phenylethane. They found that symmetrical substitution of a pair of methyls for hydrogens lowered the energy of activation by 5 kcal/mole and substitution of a pair of



phenyls for hydrogen, by 12 kcal/mole. Differences in activation energy correlated with differences in resonance stabilization energies of the radicals. Their conclusion was that high stabilization energies of the radicals lead to lower dissociation energies of the carbon-nitrogen bonds by contributing to resonance stabilization of the transition states and thus to lower activation energies.

Overberger and Di Giulio (5), based upon kinetic data, concluded that both radicals attached to the azo linkage assist in the rate-determining step. Replacement of a methyl group in azo-bis-isopropane by a phenyl group decreased the activation energy for decomposition by 4 kcal/mole. Symmetrical substitution of a pair of methyl groups by a pair of phenyl groups caused a decrease of 8 kcal/mole. The effect of groups appeared to be additive. The compound containing two α -phenylethyl groups was 37 times more reactive than the one containing an α -phenylethyl group and an isopropyl group, making it unlikely that the cleavage of the α -phenylethyl-nitrogen bond is rate-determining in both cases. They made a point of the fact that the decomposition rate depends on the entropy of activation as well as the activation energy.

Cohen and Wang (6) studied substituent effects in a series of para-substituted phenylazotriphenylmethanes. All substituents slightly decreased the decomposition rate with respect to the unsubstituted compound to varying

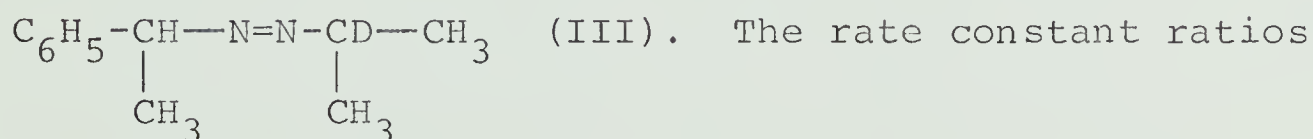
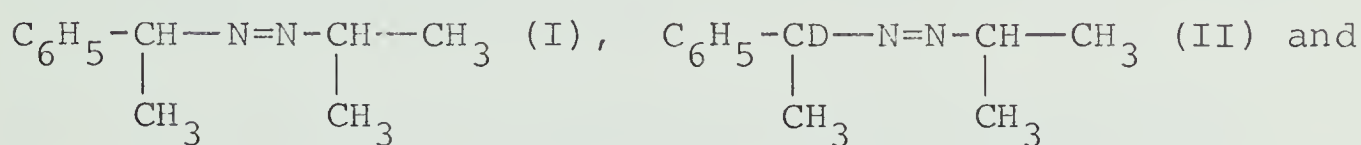
extents. While they conceded the possibility that one-bond cleavage may occur because of the great difference in strength between the triphenylmethyl-nitrogen and phenyl-nitrogen bonds, they interpreted their results as indicating that such decompositions are affected by the strength of both carbon-nitrogen bonds or by the ease of formation of both carbon radicals. The evidence was not compelling as the results could not be satisfactorily rationalized. Evidently the situation is complicated by conjugation of the azo function of the para-substituent of the phenyl ring.

In a series of papers, Seltzer established, by way of deuterium isotope effects, that there is a continuous range of decomposition mechanisms of azo compounds in solution from simultaneous symmetrical two-bond rupture to a discrete two step process. It was known from the study of SN_1 solvolysis reactions (7,8) that compounds with α -deuterium atoms at the site of substitution solvolysed 15% less rapidly than the natural compounds. Furthermore, the effects were additive so that the effect of two deuterium atoms was about twice that of one. Seltzer assumed that two α -deuterium atoms at separate reaction sites would produce an isotope effect similar to that observed for two such atoms at a single reaction site.

He measured (9) an α -deuterium isotope effect of 1.27 ± 0.03 for azo-bis- α -phenylethane which is approximately double that observed in previous unimolecular bond

scission reactions cited therein. On this basis the conclusion drawn was that the carbon-nitrogen bonds undergo simultaneous cleavage in the transition state for thermolysis.

The isotopic studies were later extended to unsymmetrical azoalkanes (10). The compounds used were derived from α -phenylethylazoisopropane:



The rate constant ratios measured were $k_{\text{I}}/k_{\text{II}} = 1.15$ and $k_{\text{I}}/k_{\text{III}} = 1.04$. The inference from these isotope effects was that both carbon-nitrogen bonds break simultaneously but that the α -phenylethyl-nitrogen bond is stretched considerably more than the isopropyl carbon-nitrogen bond in the transition state.

A more unsymmetrical azo compound, α -phenylethylazomethane was then synthesized and studied (11). The two alkyl groups, methyl and α -phenylethyl differ by about 25 kcal/mole in resonance energy (12). Substitution by deuterium in the benzylic position resulted in an isotope effect of 1.13 compared to the natural compound while for the compound containing a fully deuterated methyl group the isotope effect was 0.97. These results convincingly indicate that the rate-determining step involves only scission of the α -phenylethyl-nitrogen bond. The conclusion



was substantiated by a very small carbon-13 isotope effect in the decomposition of the same azo compound containing a carbon-13 methyl group attached directly to the azo group.

Another kinetic method for differentiating between one and two-bond scission mechanisms is the qualitative viscosity test which has been developed by Pryor and Smith (13,14). They separated initiators into two classes based on the following postulates:

- (1) Any molecule that decomposes by the synchronous scission of more than one bond breaks into too many pieces to allow cage return; such molecules will have a rate constant for decomposition that is independent of the solvent viscosity.
- (2) Any molecule that decomposes by the scission of only one bond can give cage return in solution by a simple radical combination. For such a molecule the observed rate constant for decomposition will decrease as the solvent viscosity increases, since fewer geminate pairs will separate at higher viscosities and more will undergo cage return.

The test is subject to several limitations discussed in their paper.

The azo compounds they tested by this method were p-nitrophenylazotriphenylmethane (NAT), phenylazotriphenylmethane (PAT) and azocumene. The rate constants

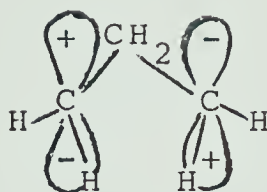


of the first two decreased in a systematic fashion going from low viscosity to high viscosity n-alkanes and 1-alkenes as solvents. The decomposition rate of azocumene was independent of solvent viscosity, indicating a concerted mechanism.

Seltzer (15) has recently reported an example of a system in which the intermediate alkylazo radical produced by a one-bond scission is so short-lived that the viscosity dependence of the observed rate constant for decomposition is masked. He found that optically active α -phenylethyl-azomethane racemized faster than it decomposed and concluded that the compound decomposes by a one-bond scission mechanism. This confirmed the conclusion he made earlier concerning this compound (11).

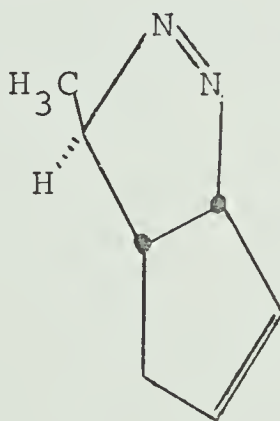
The gas phase thermal decomposition of pyrazolines has been studied by Crawford and Mishra (16). Based upon kinetic and product studies of a series of substituted pyrazolines, they suggested that the intermediate involved in the decompositions was a 1,3 cyclopropane diradical in which there was considerable interaction of the two radicals. Assuming that the intermediate trimethylene diradical is a singlet with both of its electrons in an antisymmetric orbital, conrotatory ring closing to cyclopropane would be preferred:





This rationalizes predominant single inversion of stereochemistry in the decomposition of the cis and trans isomers of 3,5-dimethylpyrazoline. By kinetic arguments it was shown that the formation of both olefins observed and cyclopropane probably proceeds through a common nitrogen-free intermediate. This work did not completely rule out a one-bond cleavage mechanism, but such a route is unlikely since cis- and trans-3,5-dimethylpyrazoline did not interconvert during their pyrolyses.

More recently, Crawford and Schneider (17) thermolysed in the gas phase a series of bicyclic azo compounds which do not readily attain the geometry required for conrotatory ring closure of a trimethylene intermediate. The structures of the compounds included were:

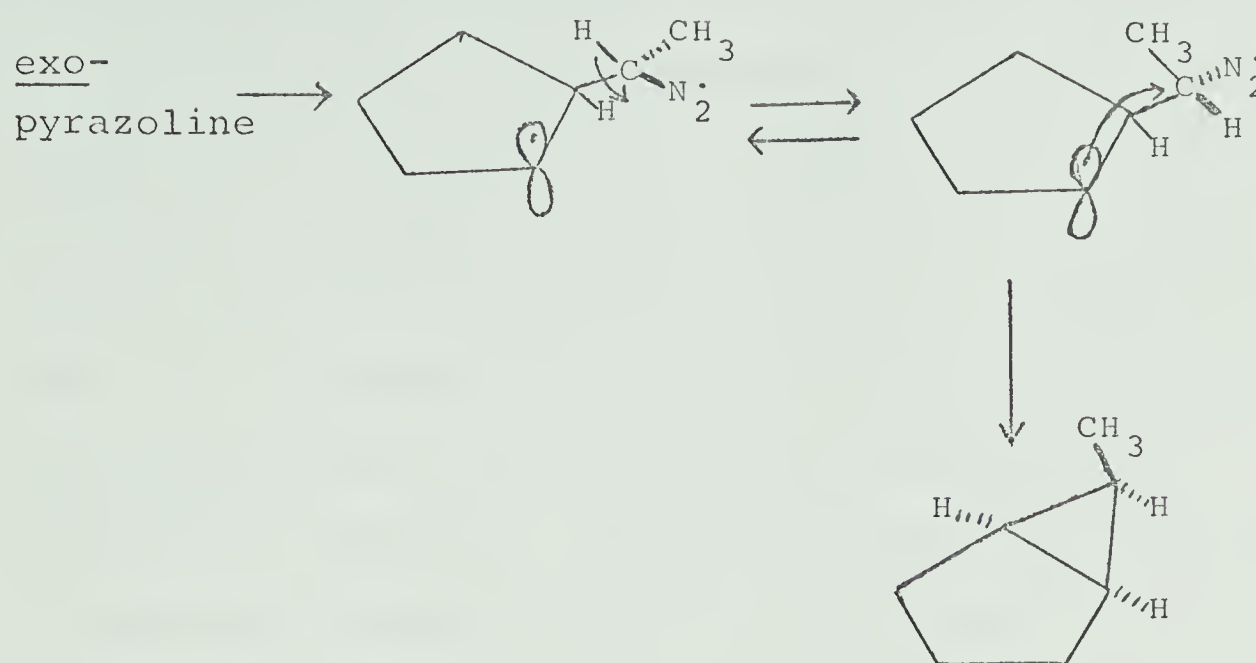




The first gave products consistent with a trimethylene intermediate. The second and third, while also giving predominate single inversion of stereochemistry in the products, gave no olefin, suggesting alternate mechanisms. Other possibilities suggested were disrotatory ring closure as a result of geometric changes in the transition state and initial formation of an inverted trigonal centre as a result of recoil associated with the breaking of two carbon-nitrogen bonds.

Bergman and Condit (18) have examined exo- and endo-2-methyl-3,4-diazabicyclo-[3,3,0]oct-3-enes and found they give predominant single inversion in the products of gas phase thermal decomposition. The increased stereoselectivity in the thermolysis of the exo compound relative to cis-3,5-dimethylpyrazoline (16) and the similar stereoselectivity in the thermolysis of the endo compound relative to trans-3,5-dimethylpyrazoline led them to the conclusion that an alternate mechanism to one involving a trimethylene species was operative. They extended a one-bond scission mechanism originally proposed by Roth and Martin (19). The scheme is outlined below:





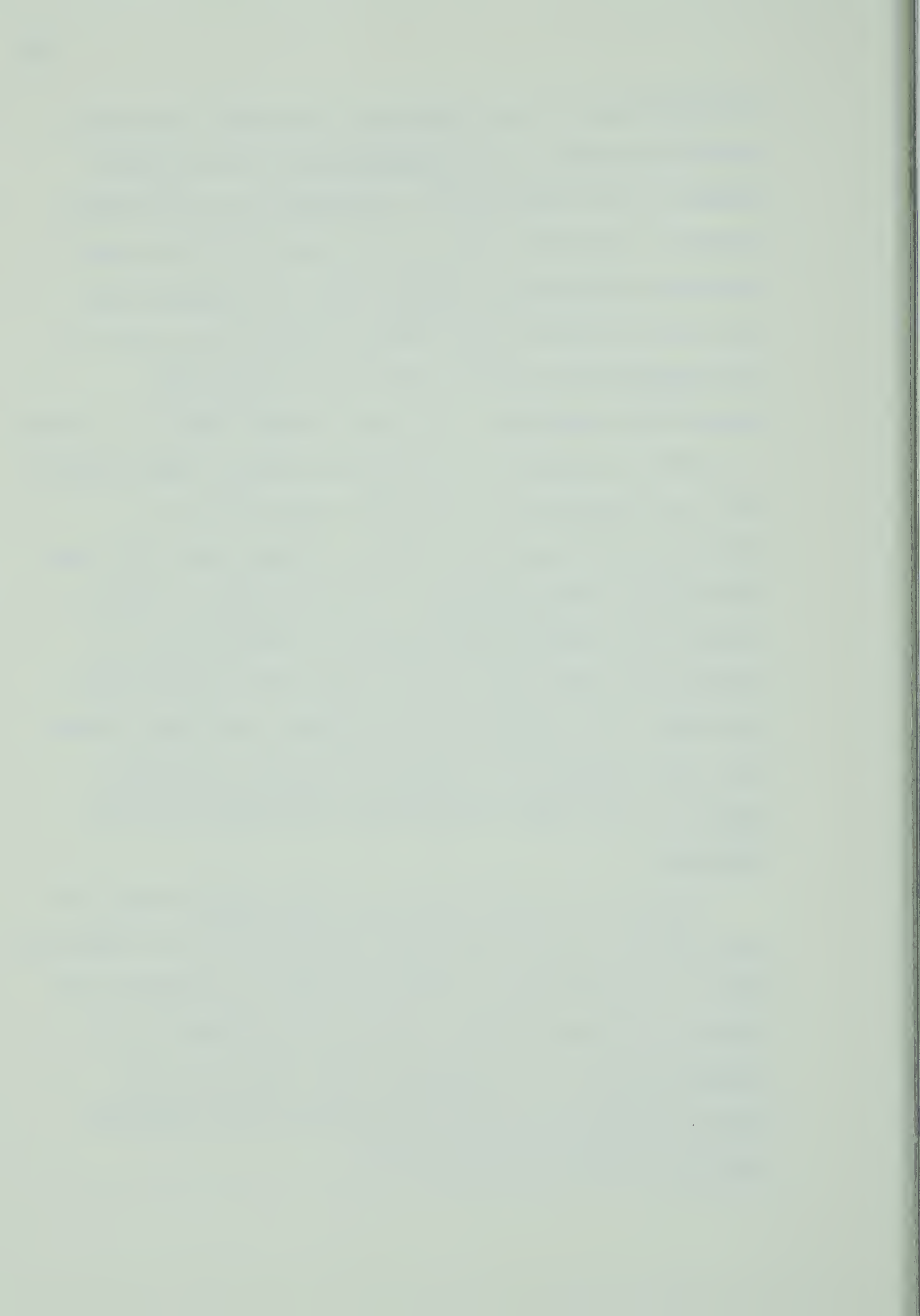
The requirement that free radical displacement must occur by backside attack (20) leads to the inverted product as observed. Unfortunately, their conclusions are based solely upon product studies. Crawford (17) had already considered such a process for similarly strained bicycloazo compounds and subsequently ruled it out by kinetic studies which included deuterium labeling.

Crawford and Takagi (21) have presented a strong case for a one-bond scission mechanism in the gas phase thermolysis of a series of acyclic azo compounds containing allyl groups. The structures of the azoalkanes studied are as follows: $\text{CH}_3\text{-N=N-CH}_2\text{CH=CH}_2$, a; $\text{n-C}_3\text{H}_7\text{-N=N-CH}_2\text{CH=CH}_2$, b; $(\text{CH}_3)_3\text{C-N=N-CH}_2\text{CH=CH}_2$, c; $\text{CH}_2=\text{CHCH}_2\text{-N=N-CH}_2\text{CH=CH}_2$, d. By using known data for the



decompositions of the symmetrical compounds azomethane, azo-bis-n-propane, azo-bis-tert-butane and azo-bis-1-propene, they predicted rate constants for the decomposition of compounds a to c on the basis of a two-bond scission mechanism by assuming that the decomposition rate of an unsymmetrical compound would be the mean of the decomposition rates of the two corresponding symmetrical compounds. They also assumed that if, instead, a one-bond scission of the allylic-nitrogen bond occurred that the decomposition rates for compounds a to c would be in the range of 0.05 to 5 times that of d, thus allowing for steric effects.~ In the absence of steric effects, the decomposition rates of compounds a to c would be one half that of d if a one bond scission was occurring. The observed rate constants were well within the range predicted by a one-bond scission mechanism and not in the range predicted by a two-bond scission mechanism.

Benson and O'Neil (22) have also supported the two-step process for the gas phase thermolysis of azo compounds. From the experimentally determined heat of formation of azo-bis-isopropane and the activation energies for the decompositions of azo compounds they calculated the heats of formation of both radicals and azo compounds using the following assumptions:



- (1) The kinetics of alkyl azo compound decompositions pertain to single bond rupture.
- (2) Group additivities are valid in the radicals as well as the parent azo compound.
- (3) The azo radical group value is not affected by the nature of the alkyl group bonded to the nitrogen opposite the radical centre.

In this manner activation energies of many azo compound decompositions were predicted accurately. The authors concluded that one-bond scission is the favoured reaction mode for all the gas phase azo compound decompositions included in their monograph.

The one-bond cleavage mechanism for the thermal decomposition of azo compounds requires the intermediacy of an alkylazo or diazenyl radical $R-N=N\cdot$. The existence of such a radical has been proposed in other reactions. Kodama (23) found that the quantum yield of low temperature photolysis of azomethane in n-hexane is smaller than unity and falls off with a lowering of temperature. He attributed this to cage recombination of initially formed methyl and methylazo radicals, mentioning that the latter must be very short-lived.

Ayscough, *et al.* (24), photolysed several azo compounds at -196° while observing the resultant e.s.r. spectra. They found evidence for an alkylazo radical

in the decomposition of azo-bis-isobutyronitrile, although the radical decomposed readily even at this temperature. Methylazo and phenylazo radicals were concluded to be even less stable, if formed at all.

Arenediazothiulates, of general structure Ar-N=N-SR are thought to undergo initial single bond scission upon thermal decomposition in solution, giving the phenylazo radical (25). The supporting evidence obtained consists of solvent viscosity rate dependence, substituent effects and the absence of an appreciable cage effect.

The phenylazo radical has been proposed as an intermediate in the photodecomposition of the azo compound phenylazo-2-phenylbutane (26). The optically active azo compound was photolysed at 25° to 40% completion. The recovered azo compound had only 75% of the optical activity of the starting material. This was accounted for by an initial one-bond scission followed by cage return of the radical pair.

In this work the acyclic azo compound chosen for study was thought likely to undergo thermal decomposition in solution by a one-bond scission mechanism. It could be easily synthesized and its asymmetric centre and that of its unsymmetrical decomposition product could be related to compounds of known configuration. It was expected to decompose at a relatively low temperature, enhancing the possibility of detecting one-bond scission. Also, the

asymmetric carbon radical produced in the decomposition of this azo compound was considerably different from those previously generated by this method.

R E S U L T S

Preparation of 1,1-diphenyl-1'-ethyl-1'-methyldiazomethane, 4

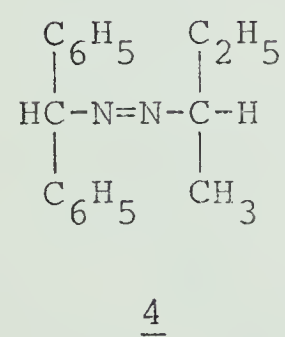
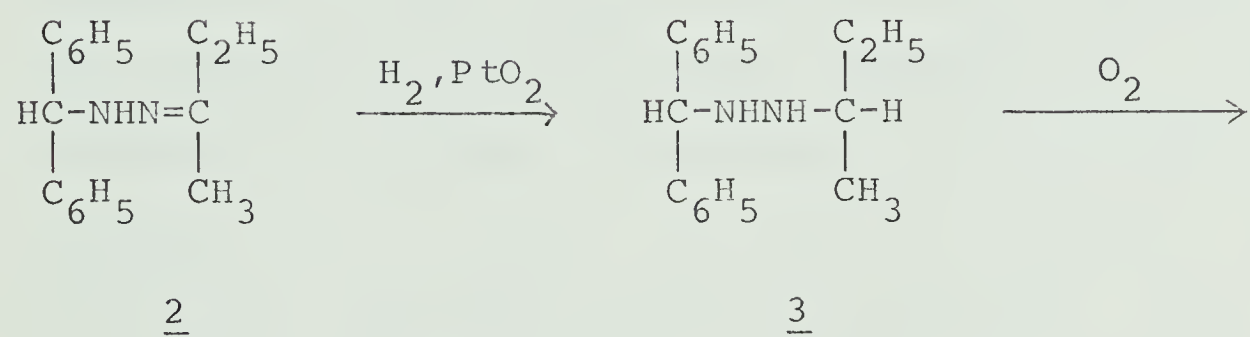
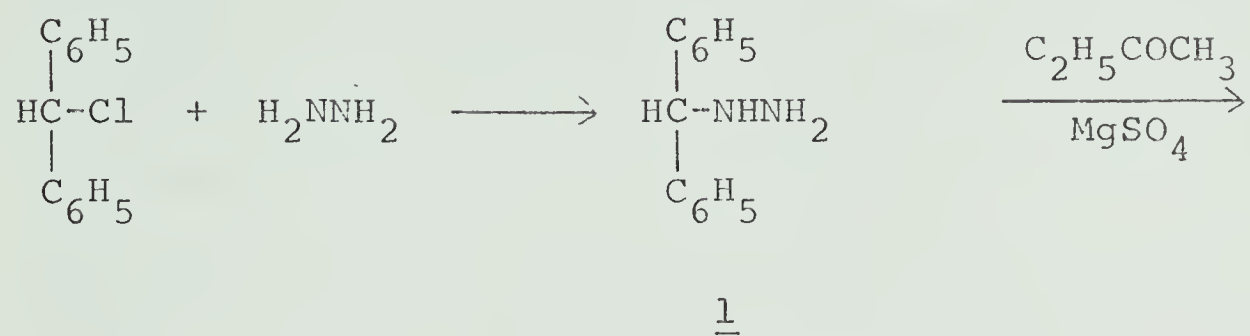
The unsymmetrical azo compound 4 was synthesized by three separate routes. The first two were designed to provide the compound in quantity and the third furnished a method for obtaining optically active material.

Method A

This method resembles the general one of Overberger (27) for synthesizing unsymmetrical azoalkanes. It was possible to use a much shorter route to the starting mono-substituted hydrazine, however. The method is outlined in Scheme I.

In dimethylsulfoxide solvent at 50°, hydrazine easily displaces chlorine from diphenylmethylchloride, yielding directly diphenylmethylhydrazine, 1. An excess of sodium bicarbonate is used to neutralize the hydrochloric acid produced. Extraction and distillation gave the pure compound in 80% yield. The identity of the product was confirmed by its n.m.r. spectrum and melting point (28).

The next step consisted of condensing the hydrazine 1 with 2-butanone in the presence of magnesium sulfate. Acid catalysis was not required; the mixture was simply heated at 50° for two hours. The yield of 2-butanone diphenylmethylhydrazone, 2 after distillation was 60%. The n.m.r. spectrum was consistent with the

SCHEME I

proposed structure.

The hydrazone 2 was readily reduced at atmospheric pressure on a microhydrogenation apparatus, using Adam's catalyst. The intermediate hydrazo compound 3 was expected to be highly susceptible to air oxidation and no attempt was made to isolate and purify it. Instead, its ether solution was stirred in air for six hours to effect oxidation to the desired azo compound 4. Good results are usually obtained by air oxidation of hydrazo compounds (1,2,29) and the method is more convenient than the conventional mercuric oxide oxidation (27). After removal of the ether, the residue was chromatographed on a short Florisil column. The pure azo compound, a pale yellow oil, was eluted rapidly by n-pentane. Use of other adsorbents such as alumina and silica gel resulted in decomposition or isomerization of the azo compound on the column. The yield from hydrazone was 25%. The azo compound was stable and could be stored for weeks at 0° without any noticeable change in its n.m.r. spectrum.

The structure of 4 was carefully confirmed by its n.m.r. spectrum in carbon tetrachloride. The aromatic protons appeared as a broad signal centred at 2.77 τ ; the uncoupled methine proton as a sharp singlet at 4.48 τ ; the other methine proton as a sextet centred at 6.54 τ ; the methylene protons as a multiplet centred at 8.35 τ and the two methyl groups as a doublet and triplet at 8.84 τ

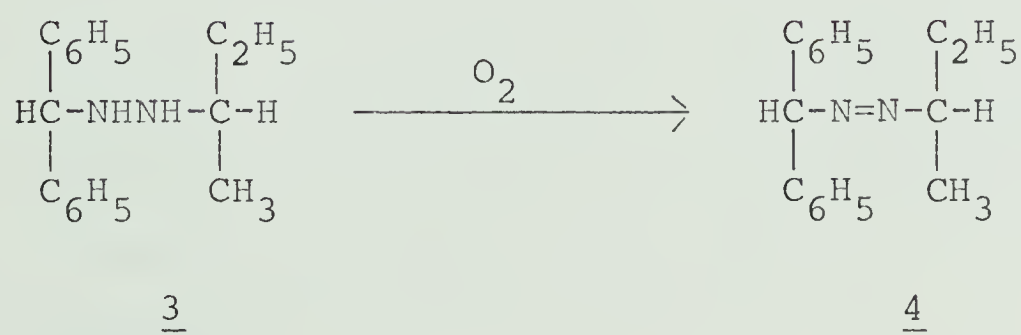
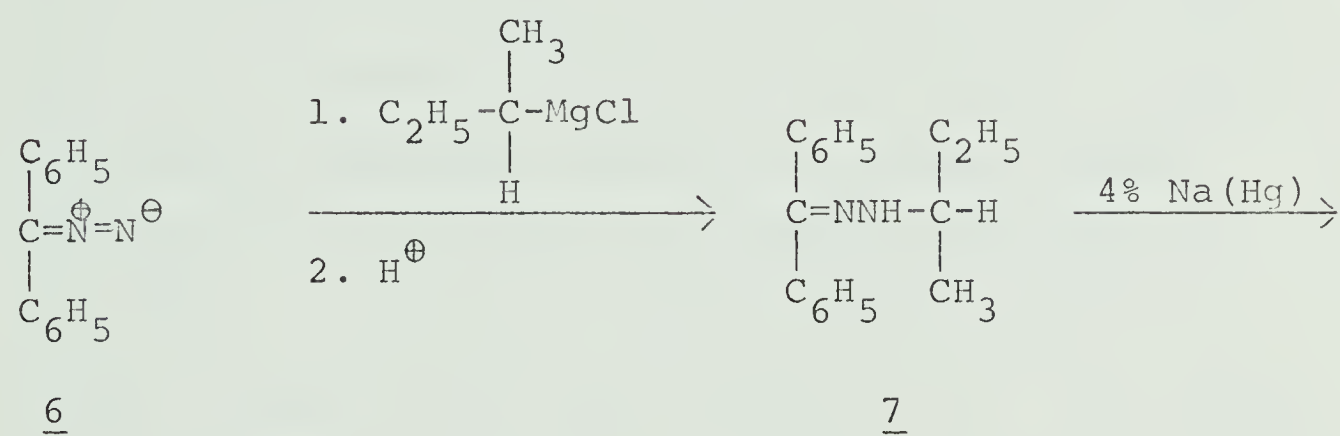
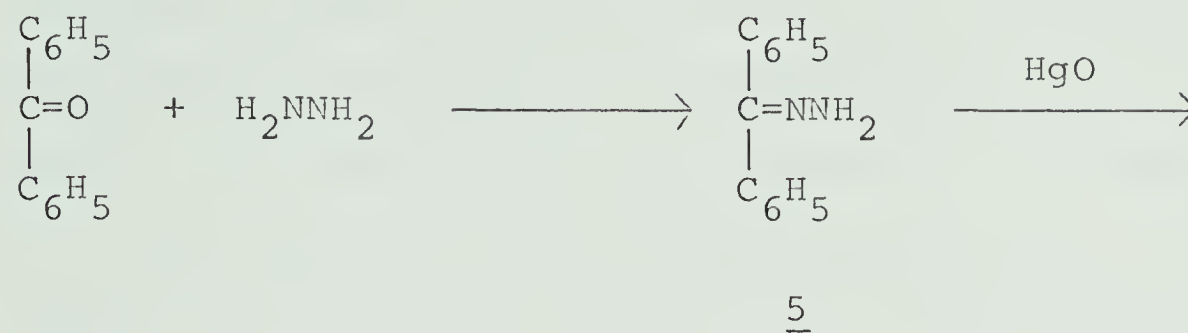
and 9.26 τ , respectively. The infra-red spectrum showed a weak absorption at 1603 cm^{-1} , characteristic of the -N=N- stretch. A satisfactory analysis was also obtained.

The hydrazone 2 could also be reduced effectively by lithium aluminum hydride in refluxing ether. After hydrolysis of the reaction mixture and oxidation of the hydrazo compound followed by chromatography there was obtained compound 4 in 20% yield, based on hydrazone. The method was less convenient than catalytic reduction. Oxidation of the hydrazo compound 3 could also be effected by silver carbonate but gave no improvement on the more easily carried out air oxidation.

Method B

This method incorporates the synthesis of a substituted benzophenone hydrazone by an adaptation of a method used by Smith, *et al.* (30), to prepare a similar hydrazone. The sequence is outlined in Scheme II.

Benzophenone was condensed with hydrazine to give benzophenone hydrazone, 5, in 70% yield, using the method of Schönberg, *et al.* (31). The purified hydrazone was converted by treatment with yellow mercuric oxide to the corresponding diazo compound 6. The method was that described in Organic Synthesis (32). Since diphenyldiazomethane is unstable it was used immediately without purification for the next step.

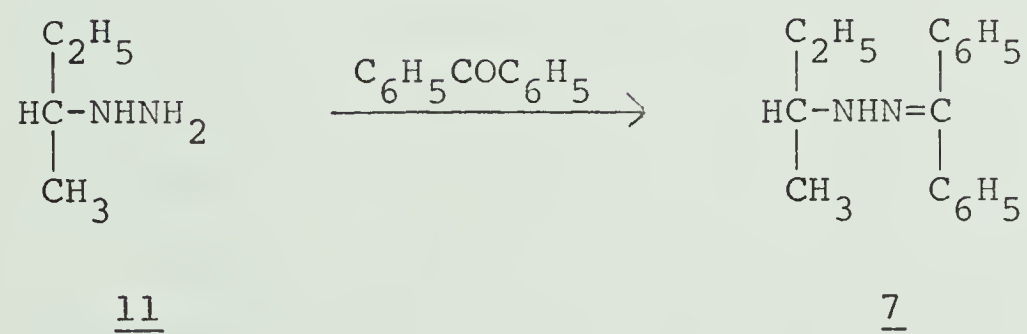
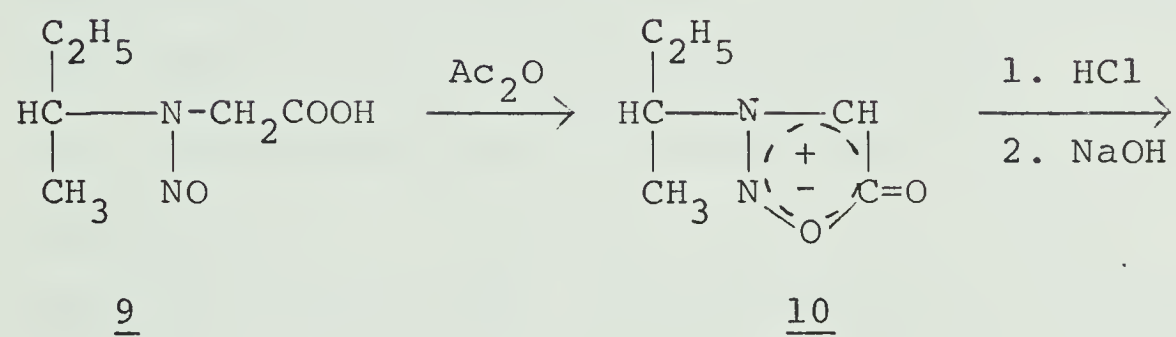
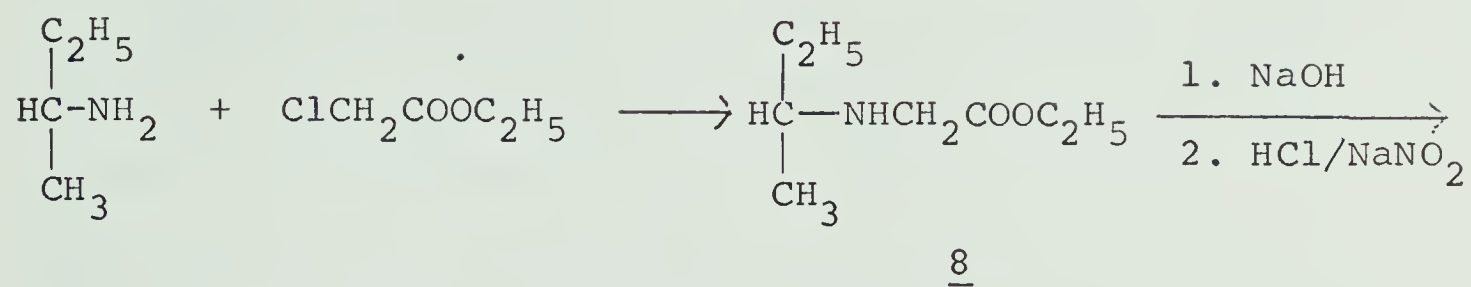
SCHEME II

The Grignard reagent, 2-butyilmagnesium chloride, was prepared in ether and an ether solution of the diazo compound 6 was slowly added. After hydrolysis of the reaction mixture and distillation of the residue there was obtained benzophenone 2-butylhydrazone, 7, in 72% yield. Its identity was confirmed by n.m.r. spectroscopy.

The hydrazone 7 proved highly resistant to reduction of the carbon-nitrogen double bond. Unsuccessful methods tried included catalytic reduction by platinum oxide, palladium on charcoal and rhodium on alumina, sodium borohydride reduction and lithium aluminum hydride reduction. In all cases, the starting material was recovered. A successful reagent turned out to be 4% sodium amalgam in ethylene glycol at 120°. The amalgam was prepared according to the method described by Feiser (33). The hydrazone 7 was reduced to the hydrazo compound 3, which was extracted from the reaction mixture with ether and oxidized by air in the usual manner. The azo compound was identical to that described previously, although the yield was low, 15%.

Method C

The object of this synthetic route was to synthesize the azo compound from 2-butylamine without affecting any of the bonds to the asymmetric carbon atom. Hence, from resolved amine, optically active 4 of known configuration and purity could be obtained. Scheme III shows the

SCHEME III



reaction sequence chosen. Compound 7 was converted to 4 as before. The S-(+)-2-butylamine used had an optical purity of 92%.

Compound 10 belongs to a class of compounds called sydnones (34). Synthesis of the hydrazine 11 via the sydnone route, although long, is justified by the relatively good yield and ease of purification of the product. The hydrazine could be produced from the amine in a one-step reaction by either chloramine (35) or hydroxylamine-O-sulfonic acid (36), but the yields are very low and the purification painstaking.

The synthesis of N-2-butylsydnone, 10, is an adaptation of the method of Greco, *et al.* (37). The reaction between ethyl chloroacetate and 2-butylamine in refluxing benzene produces 8, the ethyl ester of N-2-butylglycine. A two-fold excess of amine was used to consume hydrogen chloride produced, forming insoluble amine hydrochloride salt. Most of the excess amine could be recovered by treatment of the salt with base.

Without isolation, compound 8 was hydrolysed by refluxing aqueous sodium hydroxide and the resulting solution was treated with sodium nitrite and acidified slowly with concentrated hydrochloric acid, resulting in the substituted N-nitrosoglycine, 9. This was extracted from the reaction mixture with ether and the crude material heated with acetic anhydride to afford the

sydnone 10, which was purified by distillation. The yield was 35% based on amine and the rotation was $[\alpha]_D^{25} = +48.8^\circ (c\ 11.5, \text{CCl}_4)$. The structure was verified by n.m.r. spectroscopy.

The hydrolysis of 10 was by the method of Hunsberger, *et al.* (38), but their isolation procedure was found unsatisfactory and a better method was worked out. After heating the sydnone with concentrated hydrochloric acid until no more carbon dioxide was evolved, the resulting solution was made basic and distilled to give a mixture of hydrazine 11 and water. Potassium hydroxide pellets were used to extract most of the water and then the organic layer was distilled from barium oxide to give a colourless liquid with a typical hydrazine odour. The compound, formed in 65% yield, was identified by its n.m.r. and i.r. spectra. The rotation measured was $\alpha_D^{25} = -3.35^\circ (l, 1\ \text{dm.}, \text{neat})$.

Since in Scheme I hydrazine was able to displace chlorine from diphenylmethylchloride, an effort was made to treat 2-butylhydrazine, 11, similarly to give directly the hydrazo compound 3. Numerous attempts failed both with diphenylmethylchloride and diphenylmethylbromide under varying reaction conditions. An entirely different approach was then used instead. Benzophenone was condensed with hydrazine 11 using 1-butanol as solvent, resulting in a 30% yield of benzophenone 2-butylhydrazone, 7,

identical with a sample prepared via Scheme II. This hydrazone was converted to the azo compound 4 as before. The azo compound had a rotation $[\alpha]_D = -2.8^\circ (c\ 2.93, \text{CCl}_4)$.

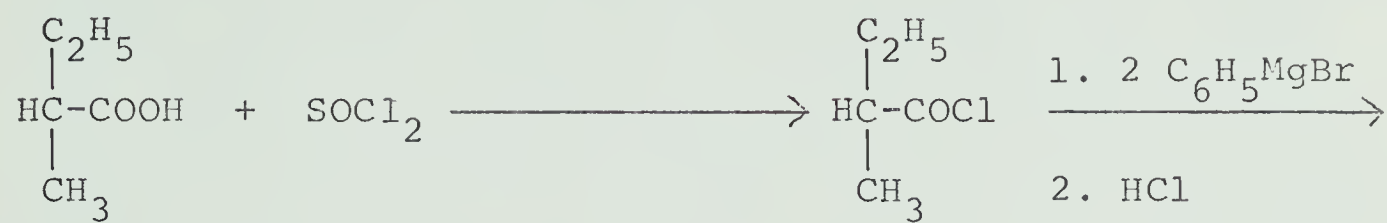
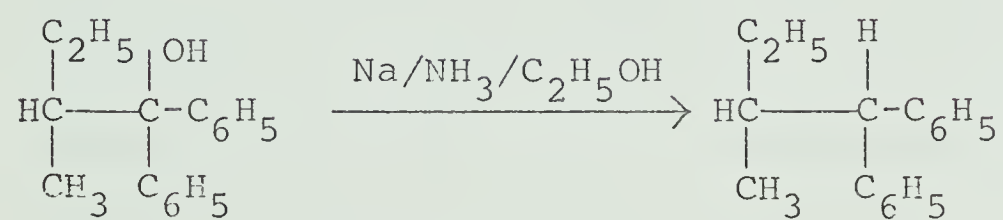
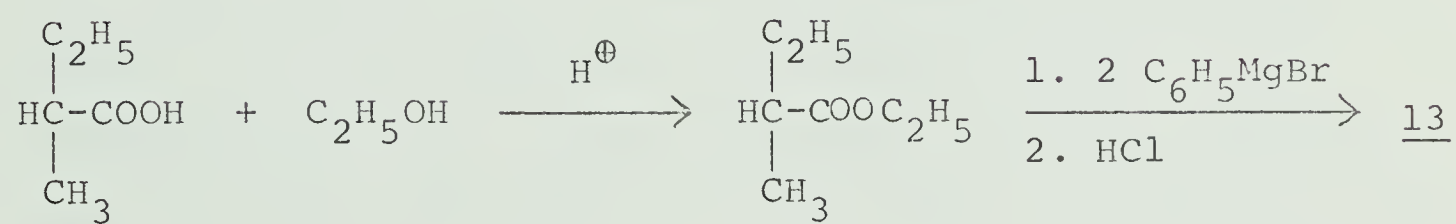
Preparation of 1, 1-diphenyl-2-methylbutane, 14

This hydrocarbon is the unsymmetrical coupling product expected from the decomposition of 4. It had to be synthesized from a precursor containing an optically active 2-butyl group of known absolute configuration without affecting the asymmetric carbon atom. Such a synthesis from the well characterized 2-methylbutanoic acid is outlined in Scheme IV. The active 2-methylbutanoic acid employed had an optical purity of 85%.

The intermediate alcohol 13 had been synthesized previously by Huston and Jackson (39) and their method was used without modification. The physical properties of the product obtained corresponded to those of the previous workers, as did the yield, 60%.

Alcohol 13 could also be synthesized by a Grignard reaction on the ethyl ester of 2-methylbutanoic acid rather than the acid chloride, but the yield was low and the product contaminated.

There are various reported techniques for hydrogenolysing benzylic alcohols. The first method tried was an adaptation of one used by Brown and Marvel (40) to hydrogenolyse some p-bromophenylalkyl carbinols. Treatment of alcohol 13 with their reagent, iodine and phosphorous in

SCHEME IV121314

acetic acid, followed by zinc failed to give the desired product and was not investigated further.

Sodium in liquid ammonia was found to be an effective reagent, giving a high yield of hydrocarbon 14. Birch (41) showed that the dissolving metal hydrogenolysis of hydroxyl groups proceeds through a carbanion intermediate so that benzylic positions are activated. The alcohol is simply dissolved in ethanol, added to a solution of sodium in liquid ammonia and the mixture stirred for one half hour before evaporating the ammonia and recovering the product. The distilled compound showed no extraneous peaks by g.l.c. and was identified by n.m.r. spectroscopy and the molecular weight determined by mass spectrometry. It had an optical rotation $[\alpha]_D^{25} = -13.8^\circ$ (c 9.43, CCl_4).

Preparation of 1,1,2,2-tetraphenylethane, 15

This compound is the expected symmetrical coupling product from two diphenylmethyl radicals formed in the decomposition of 4. It was obtained by treating diphenylmethylchloride with magnesium using ether as solvent in the usual manner for a Grignard reaction. The intermediate Grignard complex reacts with itself to form the symmetrical tetraphenylethane. Two recrystallizations of the product from ethanol gave 15, in 50% yield, as white needles, m.p. 210° [lit. (42) m.p. 211°]. The n.m.r. spectrum showed only two peaks in the ratio of 10:1 as expected.

Preparation of 2-butylhydrazine, 11

Mono-alkylhydrazines are difficult to prepare in quantity. The sydnone route shown in Scheme III is satisfactory but lengthy. For studying the conversion of 11 to azo compound it was desirable to have an easier method for making the hydrazine. This was accomplished by hydrolysing benzophenone 2-butylhydrazone, 7, with hydrochloric acid in ethanol and working up the mixture as described previously in the hydrolysis of sydnone 10. The product, formed in 65% yield, was identical with hydrazine obtained via the sydnone route. The hydrazone 7 was prepared via Scheme II. This hydrolysis method is that of Smith, *et al.* (30).

Resolution of α -phenylethylamine

This compound was required as a resolving agent for 2-methylbutanoic acid. It was in turn resolved by the method of Thielacker (43). Hydrolysis of the tartarate salt produced (-)- α -phenylethylamine: $\alpha_D^{25} = -37.52^\circ$ (l, 1 dm., neat).

Resolution of 2-methylbutanoic acid

The published procedure of Odham (44) using (-)- α -phenylethylamine as a resolving agent was employed. After six recrystallizations of the salt there was obtained upon hydrolysis R-(-)-2-methylbutanoic acid, 85% optically pure, $[\alpha]_D^{24} = -16.40^\circ$ (l, 1 dm., neat).

Resolution of 2-butylamine

This amine was resolved by the method of Fleury-Larsonneau (45) using d-tartaric acid as resolving agent. After two recrystallizations of the bitartrate salt there was recovered by hydrolysis S-(+)-2-butylamine with an optical purity of 92%, $[\alpha]_D^{25} = +7.21^\circ (l, 1 \text{ dm.}, \text{neat})$.

Decomposition kinetics of 4

The most convenient method for following the decomposition of 4 was to monitor the rate of gas evolution. The apparatus consisted essentially of a reaction vessel and a gas burette.

Since the decomposition is unimolecular the kinetic expressions are simple. The rate constant is given by

$$k_d = \frac{1}{t} \ln \frac{(V_\infty - V_0)}{(V_\infty - V_t)}$$

where t = time

V_∞ = volume of gas evolved at infinite time

V_t = volume of gas evolved at time t

A graphical plot of $\log (V_\infty - V_t)$ versus t gives a line of slope $-k_d/2.303$. The half-life is related to the rate constant by the equation

$$t_{1/2} = \frac{2.303}{k_d} \log 2$$



The term $V_{\infty} - V_0$ affects only the intercept of the graphical plot and not the slope from which the rate constant is determined.

Besides nitrogen, gases arising from the 2-butyl radical must have been evolved. Butane and butenes comprised part of the gas volume but they were absorbed rapidly by the compound di-n-butylphthalate, used in the levelling arm of the gas burette. Due to the finite rate at which the organic gases were absorbed, there is added uncertainty in the rate constants measured. The amount of azo compound decomposed is proportional to the total gas volume, so it would have been better to use a non-organic liquid in the gas burette.

Under all but one set of conditions two kinetic runs were made to ensure consistency. The rate constant was measured in cumene at 97.3° and at 77.6° in order that activation parameters could be calculated. Also, runs were made at the lower temperature in octane and hexadecane. These solvents are of similar polarity but have very different viscosities so that any viscosity effect upon reaction rate could be detected. In order to test for induced decomposition two runs were carried out at high dilution in cumene and found to give, within experimental error, the same results as for the more concentrated solutions.

Typical rate data is given in Tables I and II and the corresponding graphical plots are given in Figures I and II. Table III gives a summary of all the results obtained. The activation parameters shown were calculated in the usual manner (47) using the data from decompositions in cumene at two different temperatures. The uncertainties are liberal estimates calculated by assuming there could be a 5% error in the rate constants and then combining the errors in such a way as to give the largest deviation, e.g., the maximum k_d at 97.3° was combined with the minimum k_d at 77.6° , and vice versa.

Product analysis

Product analysis was carried out so that the cage effect could be estimated and the stereochemistry of the unsymmetrical coupling product determined in the decomposition of 4. In order to study the decomposition products, solutions of azo compound were decomposed and the resulting solutions analysed by g.l.c. The solvents used were benzene and 1 M butanethiol in benzene. Approximately 0.5 ml of a 0.2 M solution of azo compound in an ampoule was degassed and sealed off under high vacuum, then placed for at least ten half-lives in an oven maintained at a constant temperature. After cooling and opening the sealed tube, its contents were analysed directly by g.l.c.

TABLE I

Rate Data for the Decomposition of 0.5 M 4
in Cumene at 97.3°.

Time (m)	Burette reading (ml)	$V_{\infty} - V_t$	$\log (V_{\infty} - V_t)$
5	16.3	26.3	1.420
9	18.2	24.4	1.388
12	20.7	21.9	1.340
14	22.0	20.6	1.314
17	23.8	18.8	1.274
20	25.3	17.3	1.238
23	26.8	15.8	1.198
26	28.2	14.4	1.158
28	29.0	13.6	1.134
30	29.8	12.8	1.107
34	31.0	11.6	1.064
37	32.0	10.6	1.025
40	32.8	9.8	0.992
44	33.8	8.8	0.944
51	35.5	7.1	0.852
55	36.0	6.6	0.820
60	36.6	6.0	0.778
65	37.2	5.4	0.732
75	38.4	4.2	0.625
92	40.0	2.6	0.425
147	42.1	1.5	0.176
300 (∞)	42.6	-	-

$$k = 4.75 \times 10^{-4} \text{ s}^{-1}$$

FIGURE I

Plot of $\log (V_{\infty} - V_t)$ vs. time for gas evolution in the decomposition of 4 in cumene at 97.3° .

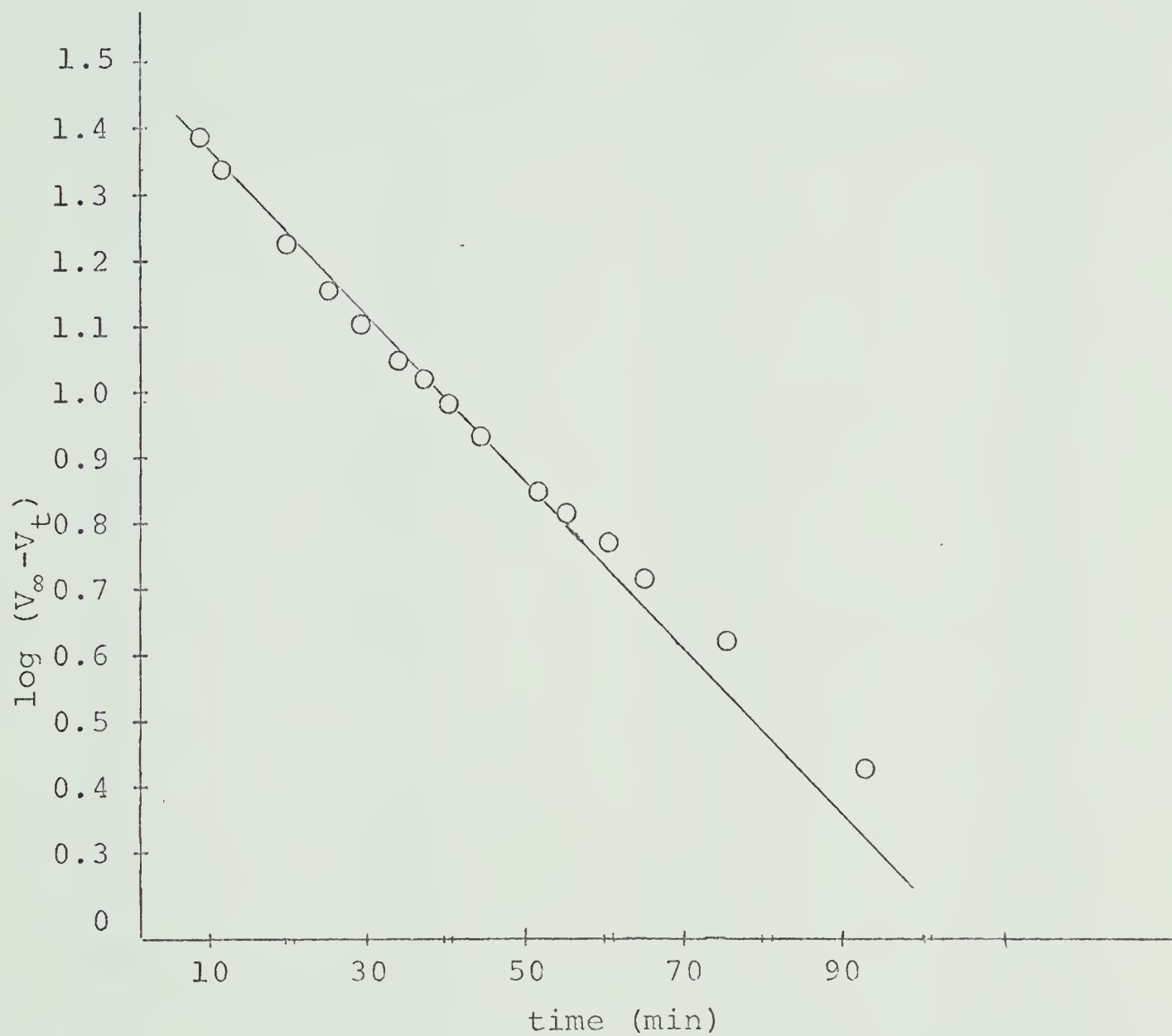


TABLE II

Rate Data for the Decomposition of 0.5 M 4
in Cumene at 77.6°.

Time (m)	Burette reading (ml)	$V_{\infty} - V_0$	$\log (V_{\infty} - V_0)$
14	19.0	23.0	1.362
21	19.4	22.6	1.354
27	19.9	22.1	1.344
36	20.3	21.7	1.336
49	21.1	20.9	1.320
63	21.7	20.3	1.307
86	23.0	19.0	1.279
106	24.0	18.0	1.255
118	24.6	17.4	1.240
133	25.3	16.7	1.224
151	26.0	16.0	1.204
178	27.2	14.8	1.170
197	28.0	14.0	1.147
226	29.1	12.9	1.111
255	29.9	12.1	1.082
279	30.7	11.3	1.054
309	31.5	10.5	1.021
452	34.8	7.2	0.850
560	36.7	5.3	0.723
1560 (∞)	42.0	-	-

$$k = 4.54 \times 10^{-5} \text{ s}^{-1}$$

FIGURE II

Plot of $\log (V_{\infty} - V_t)$ vs. time for gas evolution in the decomposition of 4 in cumene at 77.6° .

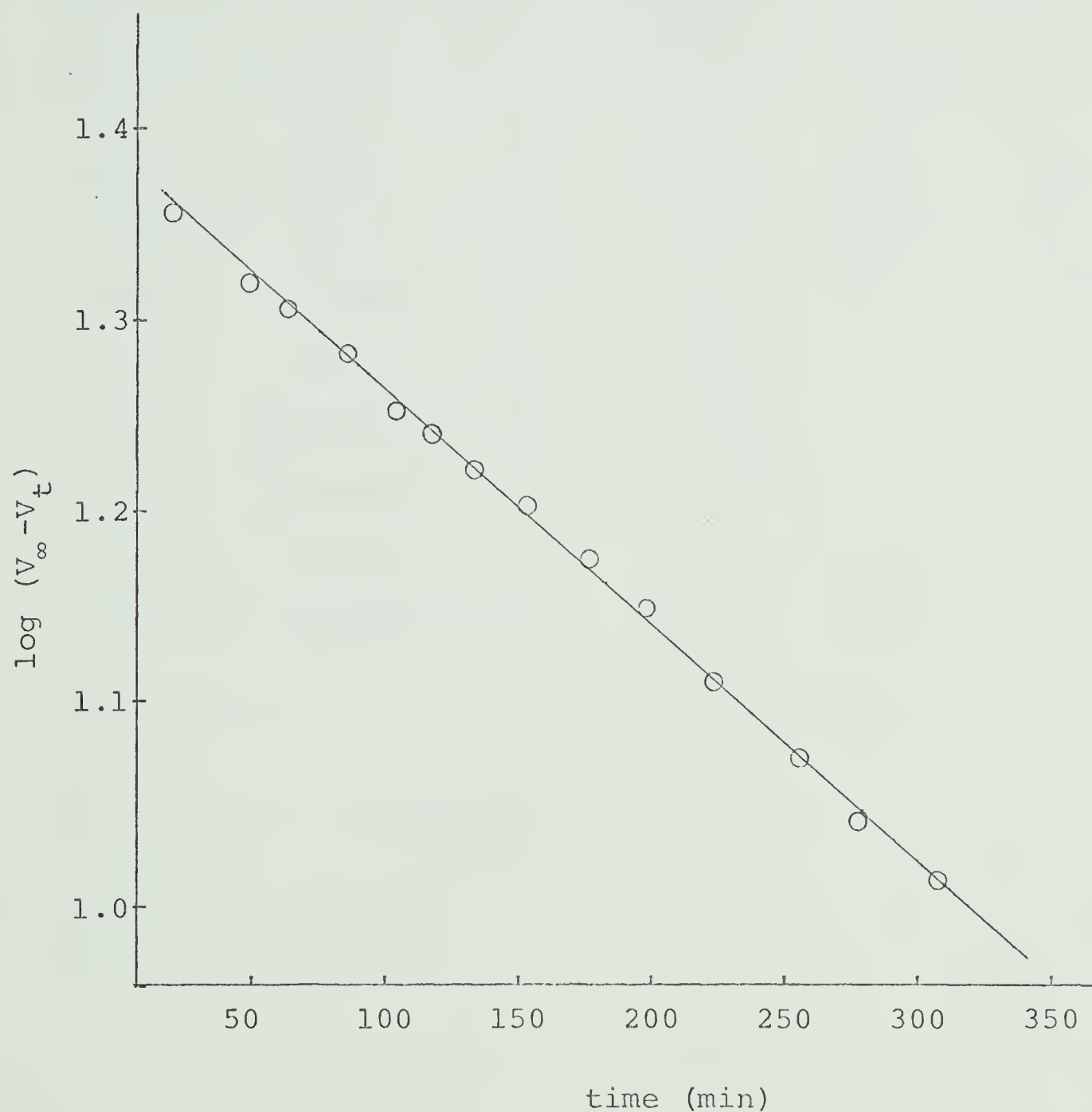


TABLE III

Summary of Decomposition Rates of 4

Temp. (°C)	Solvent	Conc. (M)	$k_d \times 10^5$ (s ⁻¹)	$t_{1/2}$ (m)	%Gas Yield
97.3	cumene	0.5	47.5	24.4	
97.3	cumene	0.5	48.7	23.8	91
77.6	cumene	0.5	4.42	26.2	
77.6	cumene	0.5	4.54		88
77.6	octane	0.5	4.28		
77.6	hexadecane	0.5	4.00		
77.6	hexadecane	0.5	3.90		
97.3	cumene	0.06	49.0	23.6	
97.3	cumene	0.06	48.8	23.8	

$$E_a = 31.2 \pm 1.3 \text{ kcal/mole}$$

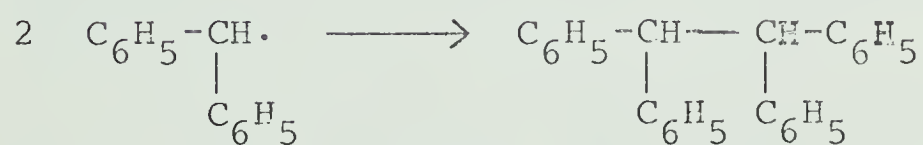
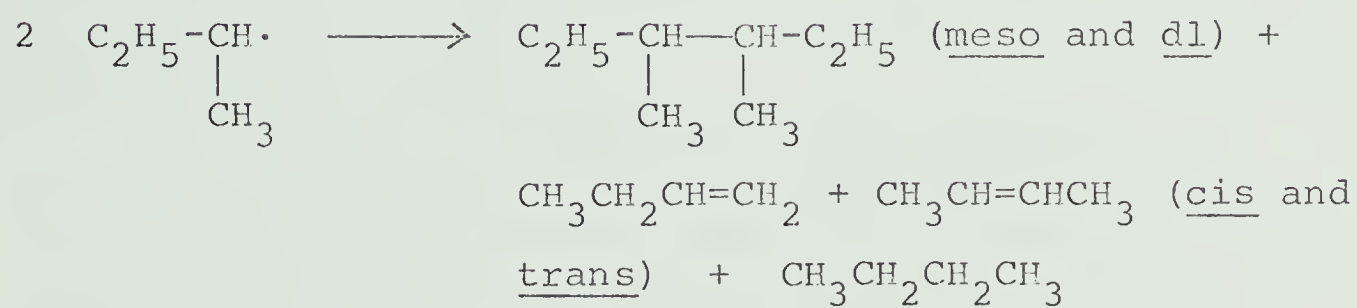
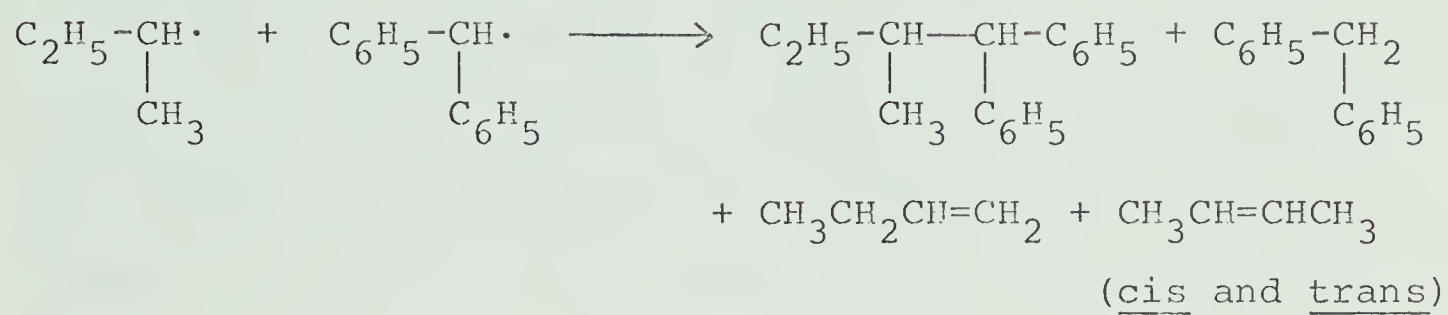
$$\Delta H^\ddagger = 30.5 \pm 1.3 \text{ kcal/mole}$$

$$\Delta S^\ddagger = 8.1 \pm 4.0 \text{ eu.}$$

The compounds expected from disproportionation or coupling between the different pairs of radicals possible were 14, 15, diphenylmethane, butane, butenes and 3,4-dimethylhexane as shown in Scheme V. Except for butane and butenes, for which no attempt at analysis was made, samples of all the expected compounds were obtained beforehand and details of their separation by g.l.c. were worked out prior to any decomposition samples being analysed. Because of the wide range of molecular weights involved, it was necessary to use two different columns: for the lighter components an 8 ft. 20% SF-96 on Chromosorb P column and for the heavier components, a 10 inch 4% SF-96 on Chromosorb P column.

Unscavenged decomposition

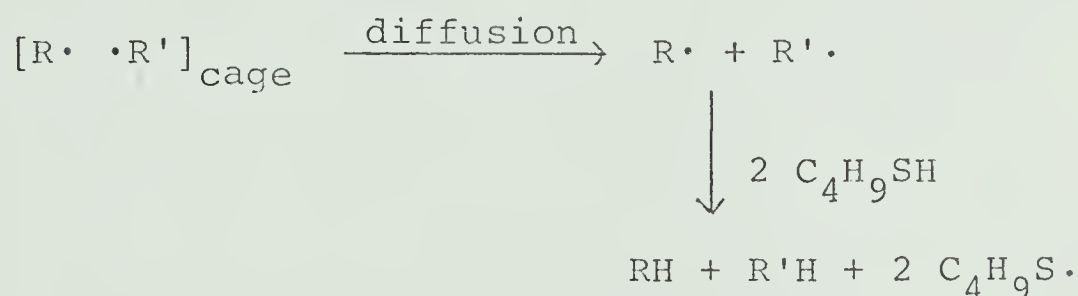
Analysis of decomposition samples revealed several unidentified small peaks which could on the basis of their retention times be assumed to be due to products which contain the diphenylmethyl fragment. There were four peaks between those corresponding to 14 and 15 and two at a greater retention time than 15. All of the expected products were observed in appreciable amounts except for 3,4-dimethylhexane, of which there was only a trace, indicating that 2-butyl radicals either reacted with solvent or reacted with each other almost exclusively by disproportionation to form butane and butenes. Thus it was

SCHEME V

impractical to determine by product analysis the fate of 2-butyl radicals. Attention was then concentrated on the distribution of compounds containing the diphenylmethyl fragment. For the purpose of calculating the cage effect the unidentified compounds were assumed to have been formed outside the solvent cage and their peak areas were combined.

Scavenged decomposition

The purpose of a scavenger was to prevent the formation of unsymmetrical coupling product outside the cage. Butanethiol accomplishes this by transferring hydrogen atoms to radicals which escape the cage, resulting in the formation of thiyl radicals:



Thiyl radicals are very stable and are consumed almost exclusively by coupling.

The diphenylmethyl radical, being very stable itself, was not completely scavenged so that although the yield of diphenylmethane increased greatly compared to an unscavenged run, there still remained a significant amount of tetraphenylethane formed. Despite this it is still valid to assume that no unsymmetrical coupling product was

formed outside the cage because 2-butyl radicals would be consumed before having an opportunity to react with diphenylmethyl radicals from other solvent cages. In the scavenged runs there were again unidentified peaks assumed to arise from compounds formed outside the cage. Two overlapping peaks occurred between those corresponding to 14 and 15. The larger of these was probably due to the product of coupling between thiyl and diphenylmethyl radicals. A further two very small peaks occurred at slightly greater retention times than that of 14.

In both the scavenged and unscavenged runs, all the compounds containing the diphenylmethyl fragment could be separated on the short SF-96 column. Response factors for the three known compounds were obtained by chromatographing mixtures of known composition followed by measuring peak areas of the chromatogram. For the unknown compounds, their response factors were arbitrarily assigned the same value as tetraphenylethane. The reasoning whereby an estimate of the cage effect was arrived at is explained in the discussion section. By using bromobenzene as an internal standard in two of the analyses it was determined that the absolute yield of products analysed for, including unknown compounds, was 67% in one case and 69% in the other. These decompositions were at 100°. The analytical results are summarized in Tables IV and V.

TABLE IV

Product Distribution of Unscavenged Decomposition
of 4 at 80° and 100°.

	diphenylmethane	Product proportions (mole %)			Cage effect
		<u>14</u>	<u>15</u>	others	
<u>100°</u>					
run 1	15	50	27	9	
run 2	13	51	25	11	
average	13.5	50.5	26	10	9.5%
<u>80°</u>					
run 1	15	49	25	11	
run 2	13	49	25	12	
average	14	49	25	11.5	10.5%

TABLE V

Product Distribution of Scavenged Decomposition
of 4 at 80° and 100°.

		Product proportions (mole %)			Cage effect
diphenylmethane		<u>14</u>	<u>15</u>	others	
<u>100°</u>					
run 1	43	18	8	31	
run 2	41	19	6	34	
average	42	18.5	7	32.5	22%
 <u>80°</u>					
run 1	35	15	4	46	
run 2	31	12	3	54	
average	33	13.5	3.5	50	17%

Decomposition of S-(-)-4

Optically active azo compound 4 was prepared from S-(+)-2-butylamine with an optical purity of 92%. The decomposition was carried out on a 0.1 M solution in benzene in a stainless steel bomb at 100° for about 15 half-lives. The solution was concentrated by distillation and the residual mixture subjected to separation by g.l.c. The unsymmetrical coupling product was collected from the effluent stream and its optical rotation was measured in carbon tetrachloride solution. An n.m.r. spectrum was taken to ensure that the hydrocarbon was pure. Another decomposition was carried out similarly in 1 M butanethiol in benzene. Comparison of the rotations of 14 recovered in the scavenged and unscavenged decompositions provided another means of calculating the cage effect. The results are recorded in Table VI.

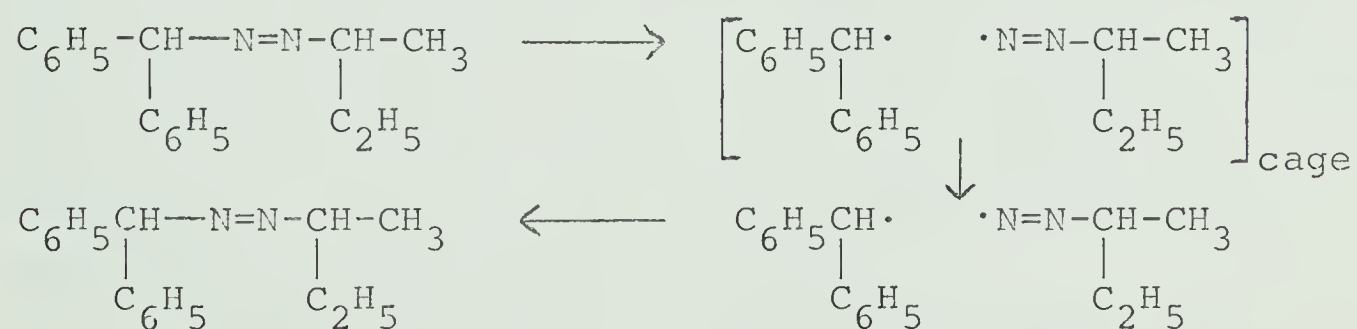
TABLE VI

Decompositions of 0.1 M Solutions of S-(-)-4 at 100°

Weight S-(-)-4 (mg)	Solvent	Isolated wt. R-(-)- <u>14</u> (mg)	$[\alpha]_D^{25}$	% Net inversion	Cage effect
700	benzene	92	-0.32°	2%	21.6%
500	1 <u>M</u> butanethiol	34	-0.90°	6%	

Chemically induced dynamic nuclear polarization (CIDNP)
in the decomposition of 4

The isolated unsymmetrical coupling product R-(-)-14 in the decomposition of S-(-)-4 had the inverted absolute configuration to that of the starting azo compound. This suggested the possibility that one-bond cleavage of 4 was occurring to produce initially a diphenylmethyl radical and a 2-butylazo radical. In a discrete step the latter would undergo β -scission to molecular nitrogen and a 2-butyl radical. If the 2-butylazo radical lived long enough to couple with a diphenylmethyl radical from another solvent cage this would give rise to a CIDNP effect (48) which could be observed on the n.m.r. signal from the diphenylmethyl proton of 4:



Decompositions in the n.m.r. probe were carried out by mixing in an n.m.r. sample tube enough azo compound with 0.5 ml of pre-heated hexadecane to give a 1 M solution, then heating the tube in the probe at 120° while continuously recording the n.m.r. spectrum. The optimum time was approximately 90 seconds after the reaction started. After about six minutes the effect was no longer observable as

the concentration of 4 and hence, of radicals, was now negligible.

The diphenylmethyl proton signal of the unsymmetrical coupling product was affected dramatically. The higher field signal of the doublet was enhanced in intensity while the lower field signal was enhanced and inverted. A transient signal, which could only be observed for the first two or three minutes occurred at about 4.0τ . In the region 5.0 to 5.5τ , enhanced as well as enhanced and inverted multiplets of uncertain origin occurred. Masked in this could have been an enhanced signal from the diphenylmethyl protons of 15. The signal intensity of the diphenylmethyl proton of 4 decreased without showing any CIDNP effect. This was seen more clearly by following the relative integration of the signal in question and the aromatic region. A spectrum of the completely decomposed solution showed signals due mainly to the compounds diphenylmethane, 14 and 15.

An attempt was made to investigate further the transient signal at 4.0τ . The peak, however, did not appear in subsequent runs although all of the other signals discussed could be observed.

D I S C U S S I O N

Syntheses

The synthesis of an unsymmetrical azo compound involves building up the structure in a multistep sequence. From the structure of 4 and knowledge of the synthetic methods available it is evident that the synthesis had to involve the intermediacy of either diphenylmethylhydrazine 1 or 2-butylhydrazine 11. No satisfactory synthesis of the latter had been reported. Its synthesis by a series of reactions analogous to that used by previous workers (27) for asymmetric hydrazines would have consisted of condensing 2-butanone with hydrazine, hydrogenating the resulting ketazine with one mole of hydrogen and then cleaving the hydrazone obtained with oxalic acid. The resulting oxalate salt of 11 would, upon hydrolysis, yield the desired hydrazone. This route could ultimately be adapted to making optically active azo compound if hydrazine 11 or the hydrazo compound 3 could be resolved.

The second approach was to make 4 from diphenylmethylhydrazine. Here, the only possibility for obtaining optically active 4 would be to resolve hydrazo compound 3. The resolution of an intermediate leaves the problem of determining the optical purity and absolute configuration of the azo compound.

It was known that hydrazine 11 could be synthesized without affecting the asymmetric centre from 2-butylamine, for which a maximum rotation and absolute configuration were well established. However, the available methods gave very low yields in this conversion so while it was necessary to eventually develop this route it was desirable to have a method available for obtaining the racemic azo compound in quantity for kinetic and product studies. Since diphenylmethylhydrazine could be made in one step, Scheme I was chosen rather than one involving the elaborate preparation of 2-butylhydrazine. The one-step synthesis of hydrazine 1 is an improvement on previous methods (4,28).

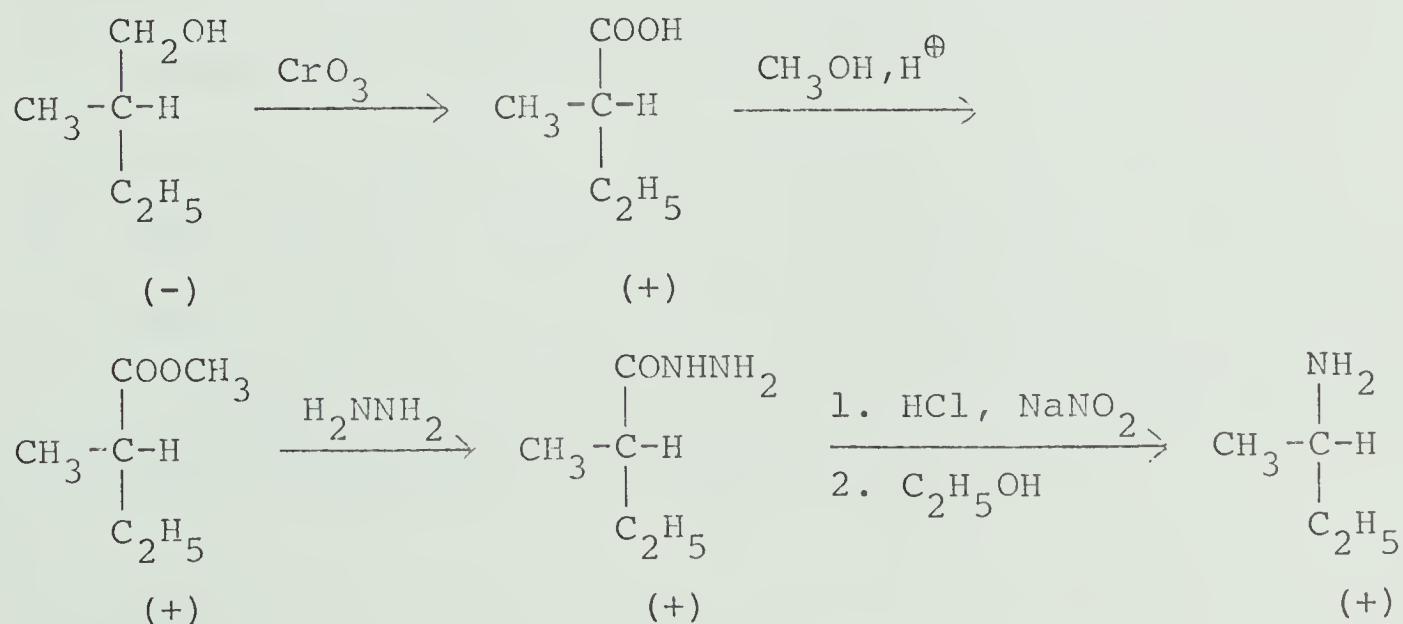
Scheme II was a convenient route to compound 7, the isomeric hydrazone of 2. Little work has been done on the reaction of diazo compounds with Grignard reagents. Some diazo compounds which have been investigated are diazomethane, phenyldiazomethane and diphenyldiazomethane (49). The last two have always given the corresponding alkylhydrazones with the Grignard reagents which have been tried: methyl, phenyl, benzyl (49) and t-butyl (30). The hydrazones obtained in the Grignard reaction can be readily hydrolysed to give the hydrazine corresponding to the Grignard reagent. This appears to be an excellent method for synthesizing mono-alkyl hydrazines. Furthermore, in the synthesis of unsymmetrical azo compounds, by selecting the appropriate diazo compound it would be possible to

eliminate two steps: hydrolysis of the hydrazone obtained from the Grignard reaction and condensation of the mono-alkyl hydrazine with a ketone.

The synthesis of S-(-)-2-butylhydrazine via Scheme III is the first example of an optically active hydrazine being obtained in this manner. The advantage over a one-step synthesis involving treatment of the amine with either chloramine or hydroxylamine-O-sulfonic acid is the relative ease in purifying the product. In the direct route the hydrazine cannot be completely freed of the starting amine.

Stereochemical studies

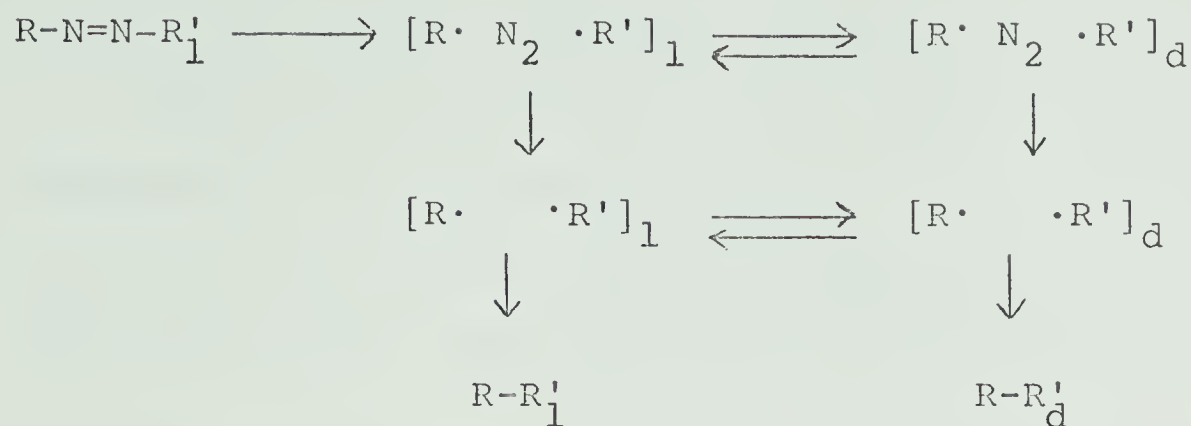
The absolute configurations of 2-butylamine and 2-methylbutanoic acid have been previously established by many methods. The most direct is that of Kjaer and Hansen (50). Starting with S-(-)-2-methylbutanol which had previously been related to glyceraldehyde (51), they made both the acid and amine by the sequence outlined below:



Besides confirming earlier stereochemical assignments, this work is particularly valuable because it shows that (+)-2-methylbutanoic acid has the same absolute configuration as (+)-2-butylamine. Thus in the decomposition of (-)-4 the stereochemical results do not depend upon correctly knowing the absolute configurations of the acid and amine.

In this investigation, (+)-2-butylamine was converted to the azo compound (-)-4. The coupling product (-)-14 was made from (-)-2-methylbutanoic acid. From the decomposition of (-)-4 was isolated (-)-14. Since (-)-2-methylbutanoic acid has the opposite configuration to (+)-2-butylamine, there was net inversion of configuration.

In previous decomposition studies of optically active unsymmetrical azoalkanes (1,2), the isolated unsymmetrical coupling product had the same absolute configuration as the starting compound. In a two-bond scission mechanism, the two carbon radicals are generated simultaneously and so long as they remain inside the solvent cage, they exist in an asymmetric environment, regardless of any considerations regarding the geometry of the radicals. Coupling inside the cage gives net retention of configuration. The retention is only partial as a racemization process occurs: rotation of the asymmetric radical prior to coupling inside the cage produces a molecule of inverted configuration:



The decomposition of S-(-)-4 is unique in that the isolated unsymmetrical coupling product has the inverted configuration with respect to the starting material. Complete racemization is the maximum effect that rotation of two simultaneously produced carbon radicals can produce. This fact is evident from an equation derived by Kopecky and Gillan (52):

$$\frac{\text{retention}}{\text{inversion}} = 1 + \frac{k_c + k_{\text{disp}} + k_{\text{diff}}}{k_r}$$

where k_c = coupling rate constant for the two radicals

k_{disp} = disproportionation rate constant

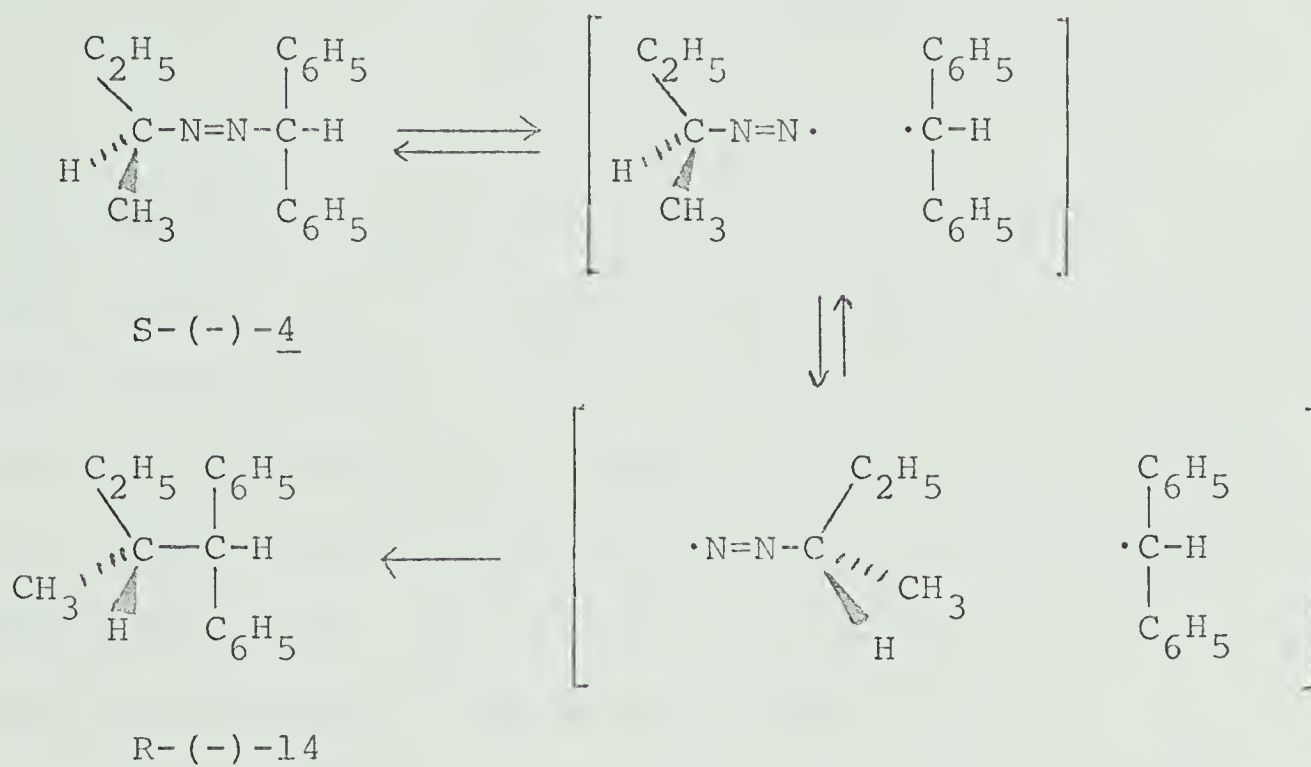
k_{diff} = diffusion rate constant of radicals from the cage

k_r = rate constant for relative rotation of the radicals.

The increased specific rotation of R-(-)-14 in the presence of a scavenger indicates that the inversion process is intramolecular. If attack on S-(-)-4 by a diphenylmethyl radical were involved in the inversion

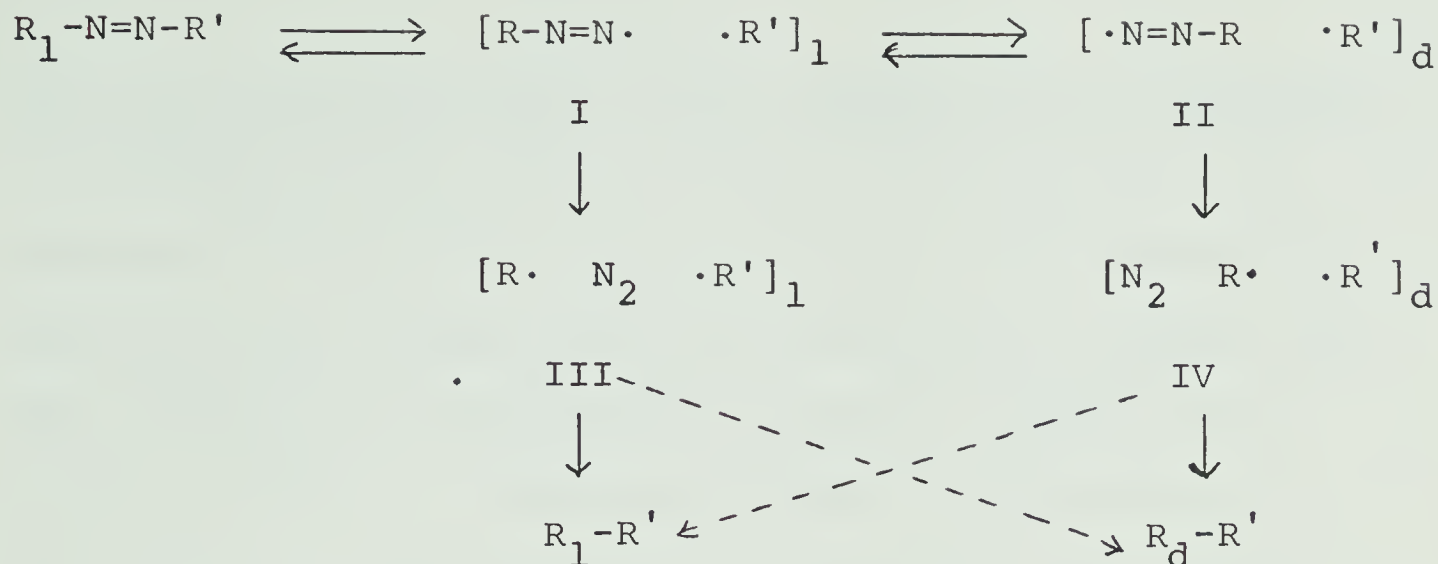
process, the radical scavenger would retard the process.

One way of accounting for the results of the decomposition of optically active 4 is by a one-bond scission followed by a radical displacement on the 2-butylazo radical. The situation is depicted below:



This inversion mechanism requires a radical displacement on carbon, a process of which there are no unambiguous examples. The special circumstances which make it feasible in this case are the high energy intermediates involved and the formation of the very stable nitrogen molecule.

It is not necessary to invoke a radical displacement to account for the inversion observed. An alternate explanation is summarized in the simplified scheme drawn below:



The alkylazo radical in I can undergo β -scission to give III. The configuration III produces net retention of configuration in the coupling product, although the retention is only partial. Alternatively, rotation of the alkylazo radical in I results in II, which gives rise to configuration IV upon β -scission. From IV there is net inversion of configuration relative to the starting azo compound.

The feasibility of obtaining inversion by this mechanism depends essentially upon two factors. First, the radical pair IV must have a significantly greater coupling to rotation rate ratio than III. This is possible because the radicals in IV are not initially separated by a nitrogen atom as they are in III. Secondly, most of the alkylazo radicals will undergo β -scission in configuration I. In order to undergo β -scission in configuration II, rotation must occur first. The greater the ratio of rotation to β -scission, the greater the fraction of alkylazo radicals that decompose in configuration II. For example if the ratio of rotation to β -scission were 1:1

then two-thirds of the alkylazo radicals would decompose in configuration I and one-third in configuration II, whereas if the ratio were 2:1, the relative proportions would be about three-fifths and two-fifths, respectively. The formation of unsymmetrical coupling product from configuration II is enhanced because recombination of the radicals cannot occur as it can with configuration I. The experimental evidence cannot distinguish which mechanism for inversion actually occurs.

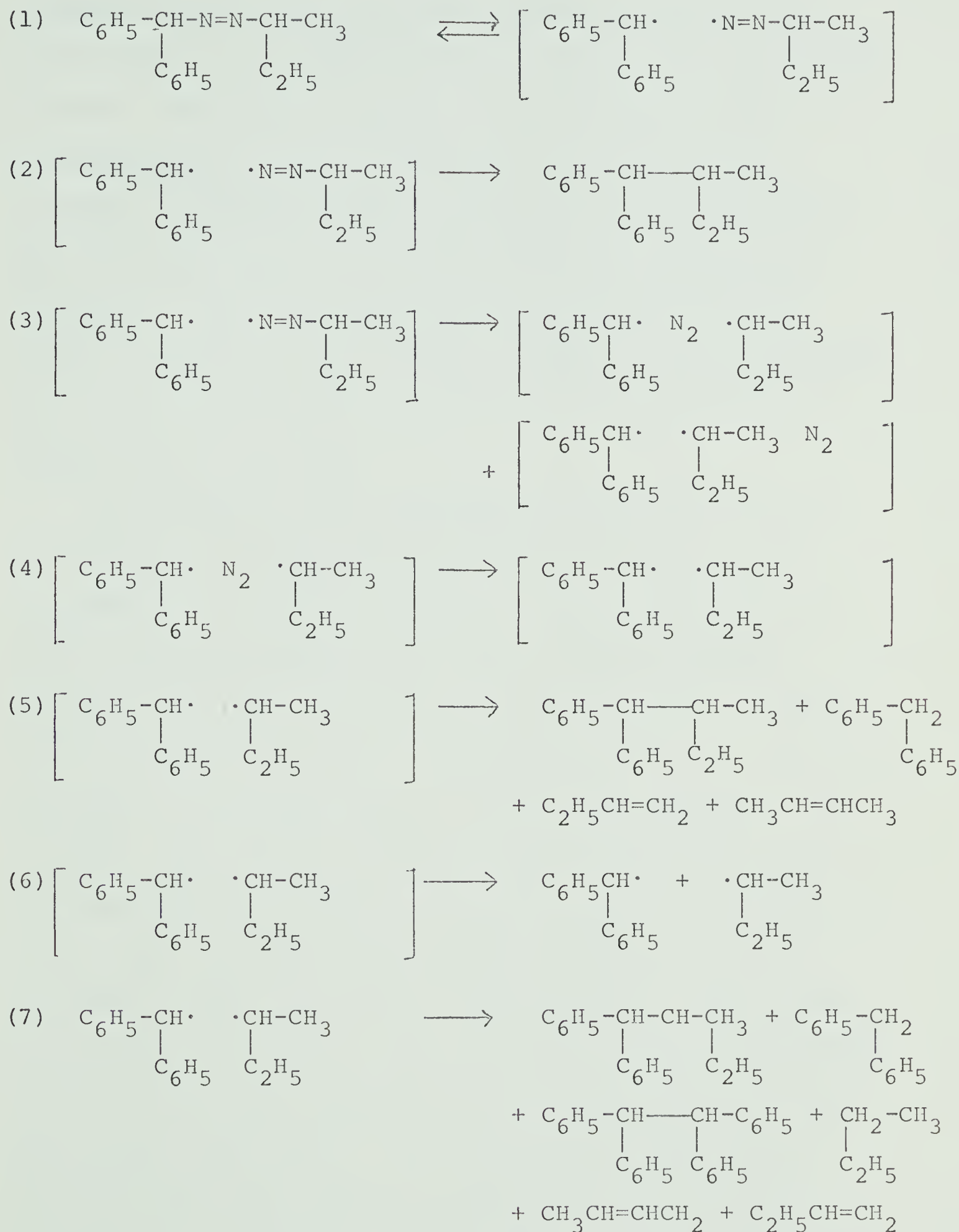
Decomposition of 4

Scheme VI represents the decomposition of azo compound 4. The brackets represent solvent cages. From the CIDNP experiments it is known that the β -scission of the 2-butylazo radical is rapid enough that it does not exist outside the primary solvent cage long enough to react with any other radical. It can be treated as a species which exists only in the solvent cage.

Radicals which have escaped the solvent cage behave independently so that statistically for every encounter of a pair of 2-butyl radicals there will be one encounter of a diphenylmethyl pair and two encounters of a diphenylmethyl-2-butyl pair. Product analysis was concerned only with the fate of the diphenylmethyl radicals.

It is assumed that all radicals react at the same rate and that all the radicals are accounted for by the products analysed. A reaction between diphenylmethyl and 2-butyl

SCHEME VI



radicals would result in either diphenylmethane or 14, while between two diphenylmethyl radicals only 15 could be formed. Therefore outside the cage one half of the diphenylmethyl radicals should be manifested in the products as diphenylmethane and 14 and the other half as 15, since 15 contains two diphenylmethyl fragments per molecule. From the amount of diphenylmethane and 14 found in excess of this ratio, the amount of cage combination can be calculated, as only these two products are formed inside the cage.

In practice, some unidentified compounds reckoned to contain the diphenylmethyl partial structure were detected in the product analysis. They are assumed to have been formed outside the cage. Their formation decreases the amount of the three known products outside of the cage so an estimate was made of them and a correction applied to the total amounts of the other products. For example, the ratio of products given in Table IV, run 2, at 100° are diphenylmethane and 14, 64; 15, 25 and others, 11. Since there are two diphenylmethyl fragments in each molecule of 15, the ratio becomes 64:50:11. Half of the last number is added to the first two numbers as explained above so that the corrected ratio of diphenylmethane and 14 to 15 is 69.5:55.5. The cage effect is therefore obtained from the amount of diphenylmethane and 14 in excess of the amount of 15 divided by the total amount of

products containing the diphenylmethyl fragment:

$$\frac{69.5 - 55.5}{69.5 + 55.5} \times 100 = 11.2\%$$

In scavenged decompositions butanethiol transfers hydrogen atoms to radicals escaping the solvent cage, resulting in compounds which can be quantitatively determined. Thus, in principle, the cage effect is calculated in this case by comparing the amount of diphenylmethane with 14 after a correction has been applied for the amount of diphenylmethane formed by disproportionation in the cage.

The situation was complicated by the fact that the diphenylmethyl radical was not trapped quantitatively so that in the scavenged runs, 15 persisted to a small extent. Also as in the scavenged runs, unidentified products containing the diphenylmethyl fragment were formed. An estimate of the cage effect could still be made, however, by assuming that the scavenger effectively quenched all 2-butyl radicals thus eliminating the formation of 14 outside the cage. The cage effect was then calculated by comparing the total number of equivalents of diphenylmethyl-containing products to the number of equivalents of 14 formed in the decomposition of 4. The ratio of coupling to disproportionation for the diphenylmethyl-2-butyl radical pair measured in the unscavenged runs was used to correct for the amount of diphenylmethane

formed by disproportionation inside the cage during a scavenged run.

A third independent method of calculating the cage effect is provided by comparison of the optical rotation of R-(-)-14 from the scavenged and unscavenged decompositions of S-(-)-4 (53). It is assumed that there is random coupling of radicals once they have escaped the cage. The fraction of 14 formed inside the cage, F , is given by

$$F = \frac{[\alpha]_{\text{D without scavenger}}}{[\alpha]_{\text{D with scavenger}}}$$

The amount of products formed outside the cage would be: 14 and diphenylmethane, $1-F$; 15, $(1-F)/2$; butane, butenes and 3,4-dimethylhexane, $(1-F)/2$. The percent cage effect is therefore given by

$$\% \text{ cage effect} = \frac{F}{2(1-F)+F} \times 100$$

The value obtained is 21.6% which is in agreement with the results from product analysis. Here, however, the result is based upon only one compound and is less reliable. The formula neglects the small amount of diphenylmethane formed inside the cage. Also, outside the cage there are compounds formed other than those considered, an additional source of error in F . These errors result in an over-estimation of the actual cage effect by this method.

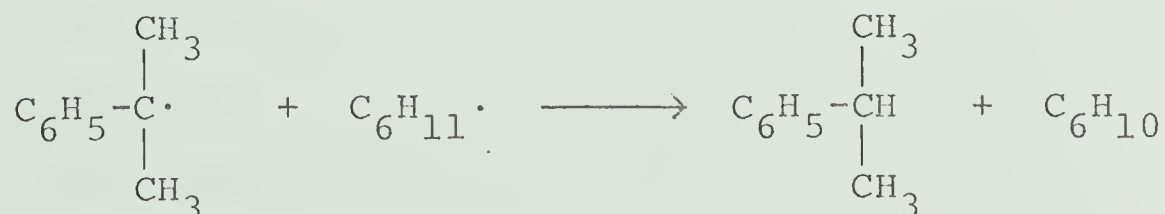
The cage effect as measured by product analysis was about 10% in unscavenged runs and about 20% in scavenged runs. The low cage effect is consistent with a one-bond scission mechanism as the initially formed radical pair can diffuse apart before any cage product is formed. The discrepancy between the two methods is not likely due to experimental error as experiments done at different times gave consistent results. The method of estimating the unknown compounds could not have led to such a difference. By arbitrarily assuming a minimum response factor for the unidentified compounds, the cage effect was maximized in all cases. Had a maximum response factor been used, the calculated cage effect would be lowered by 1% for the unscavenged runs and by 3% for the scavenged runs. The cage effect may have been underestimated in both cases by assuming that 4 decomposed exclusively by the normal unimolecular process. Some of the unidentified products may have arisen in other ways so that they should not have been included as non-cage products. However, this could not have a significant effect on the difference between the calculated values for unscavenged and scavenged runs.

The disagreement between the two methods may be more fundamental in nature. It may not be valid to assume that all radical-radical couplings occur at the same rate. If there is an appreciable difference in reaction rate

for different possible radical pairs in the case of the decomposition of 4, it could account for the lower cage effect calculated in the unscavenged runs because 2-butyl radicals would react with themselves with greater efficiency than with diphenylmethyl radicals, thereby resulting in a lower yield of diphenylmethane and 14 than expected on the basis of statistical coupling of radicals.

Bartlett and McBride (54) have correlated coupling rate constants and the cage effects observed in the decomposition of symmetrical azo compounds. For azomethane they quote a cage effect of 78% and a coupling to diffusion ratio of 3.5. For azo-bis-diphenylmethane the figures are 56% and 1.25. This casts some doubt on the assumption that outside the cage the different radical pairs in the decomposition of an unsymmetrical azoalkane will all react at the same rate.

The measured ratio of disproportionation to coupling, $k_{\text{dis}}/k_{\text{comb}}$ for the diphenylmethyl-2-butyl radical pair was 0.29. This value was obtained by comparing the amount of diphenylmethane to the amount of 14 formed in unscavenged decompositions of 4. Neumann (29) found a ratio of 0.24 for the reaction



After a statistical correction for the number of abstractable hydrogen atoms, the ratio $k_{\text{dis}}/k_{\text{comb}}$ is 0.06 in both cases. This is not surprising as Kraus (55) has shown that the ratio of disproportionation to coupling for three different butyl radical pairs correlates exactly with the number of β hydrogen atoms. In the decomposition of 4, the observed low yield of coupling product from a pair of 2-butyl radicals is consistent with the high ratio of disproportionation to coupling observed by Kraus for the 2-butyl radical pair.

Only normal coupling and disproportionation reactions of the radicals are considered in Scheme VI. In explanation of the unidentified compounds detected in decomposition mixtures there are many reactions which could conceivably occur. In one resonance form the unpaired electron of the diphenylmethyl radical is localized at the para position of a phenyl group. Para coupling would give rise to products of the quinoid structure which would aromatize upon gas chromatography:

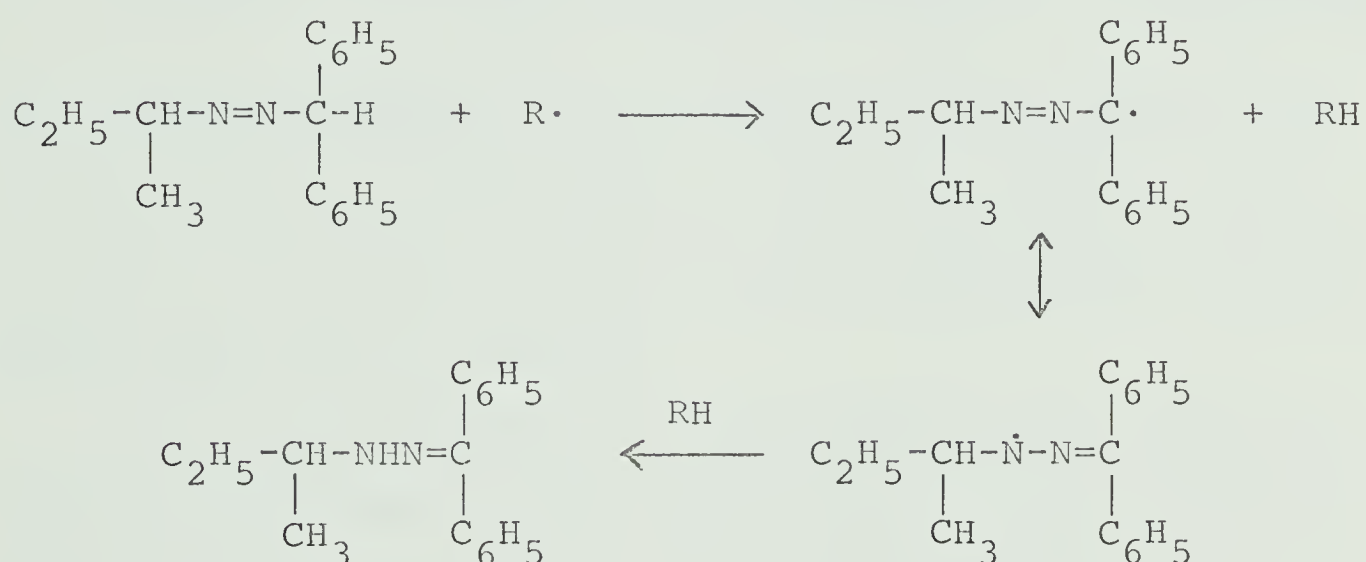


Such para-coupled product has been isolated by Pryor (13) in the decomposition of p-nitrophenylazotriphenylmethane

Ring substitution products formed with the solvent benzene are also possible in unscavenged decompositions,

especially by the high-energy 2-butyl radical. The aromatic substitution product 2-butylbenzene was not looked for by g.l.c. Its formation could explain the lower cage effect measured in unscavenged decompositions, as the consumption of 2-butyl radicals would reduce the amount of 14 formed while increasing the amount of 15.

Isomerization of 4 to a hydrazone can be envisaged by the following process:



Alternatively the radical formed by initial abstraction could couple at either the carbon or nitrogen atom. An analogous process could occur by abstraction of the methine proton of the 2-butyl group of 4.

There were also several unidentified products in the butanethiol scavenged runs. Cohen and Wang (56) have demonstrated by radioactive labelling that mercaptans catalyse free radical exchange reactions. First they thermally decomposed azo-bis-diphenylmethane in carbon-14 labelled diphenylmethane and found only a trace of

radioactivity in the product, tetraphenylethane. The exchange occurring was slower than dimerization:



In the presence of 0.035 M thiophenol, a lower energy pathway to exchange was provided:

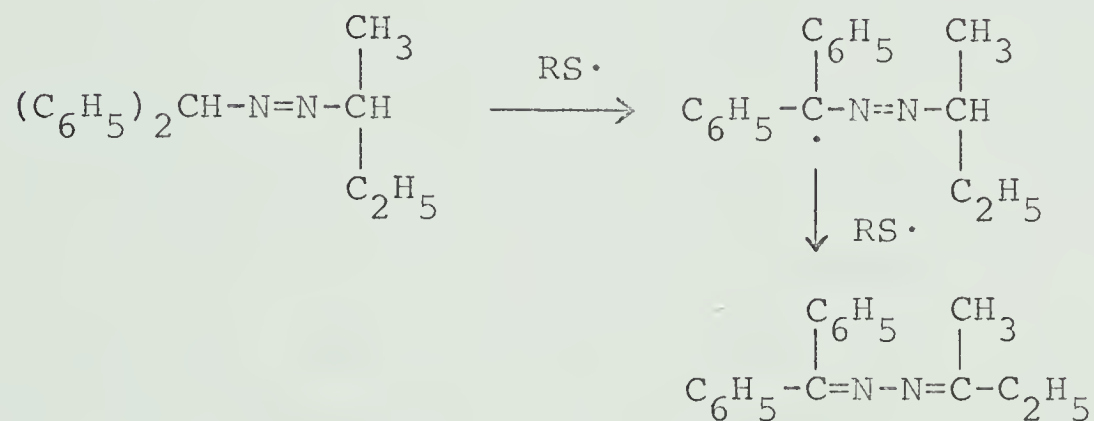


The dimerized product in this case contained 17% of the radioactivity of the solvent. They also found a large amount of product resulting from the coupling of diphenylmethyl with thiyl radicals.

In the chromatograms of the scavenged decomposition mixtures there was a peak, identified by mixed injection with an authentic sample, as di-n-butylsulfide. At a retention time between that of 14 and 15 was a large peak attributed to the coupling product of diphenylmethyl with butanethiyl radicals, although this was not proven. Overlapping this peak was a smaller one of unknown origin. Several other peaks were negligibly small. No compounds with retention times greater than that of 15 were detected.

Hydrogen atom abstraction could occur from any species present which contains a diphenylmethyl fragment.

Abstraction of a hydrogen atom from 4 would generate a free radical which could react in several ways. Being quite stable, it could live long enough to couple with any radical present, giving a new azo compound which would eventually decompose, forming new radicals and hence a greater variety of products. Azone formation could occur as follows:



This dehydrogenation occurs extensively in the octanethiol scavenged decomposition of 1,1'-diphenylazomethane (57).

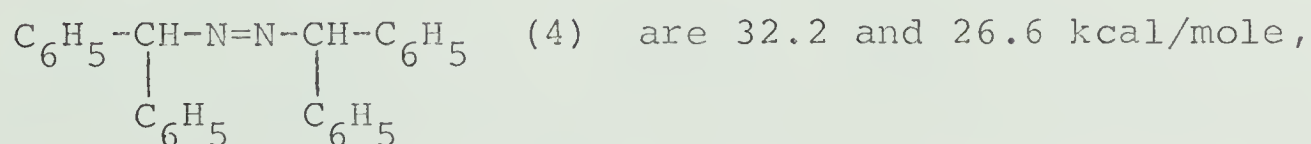
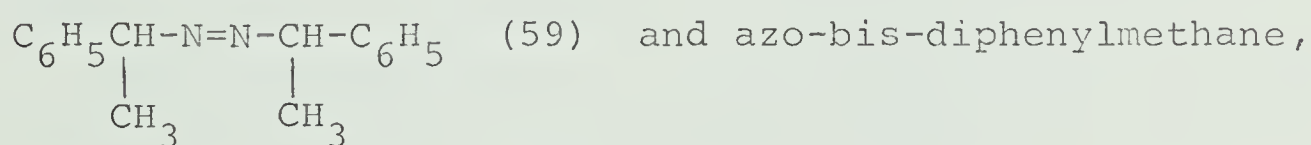
An analogous hydrogen abstraction from 14 could occur and slightly reduce the observed amount of unsymmetrical coupling product. Such abstraction from hydrocarbons by thiyl radicals has been reported (58). Abstraction of the benzylic proton would not result in any racemization of the product in the decomposition of S-(-)-4.

Kinetics of the decomposition of 4

First order kinetics were observed in the decomposition of 4. At 97.3° in cumene, the observed rate

constant was $4.81 \times 10^{-4} \text{ s}^{-1}$ and at 77.6° , $4.48 \times 10^{-5} \text{ s}^{-1}$. The similar rates observed at high dilution at 97.3° indicate that no significant amount of induced decomposition occurred. The activation parameters calculated were E_a , $31.2 \pm 1.3 \text{ kcal/mole}$; $\Delta H^\ddagger$, $30.5 \pm 1.3 \text{ kcal/mole}$ and $\Delta S^\ddagger$, $8.1 \pm 4.0 \text{ e.u.}$

The activation energy of 31.2 kcal/mole is considerably less than the value of 38.6 kcal/mole for the decomposition of α -phenylethylazomethane, also thought to decompose by a two-step mechanism (11). The kinetics for α -phenylethylazomethane were done in the solvent diphenyl ether. If both compounds decompose by a two step mechanism, less difference between the activation energies might be expected as the activation energies for the decompositions of the symmetrical compounds, 1,1'-diphenylazoethane,



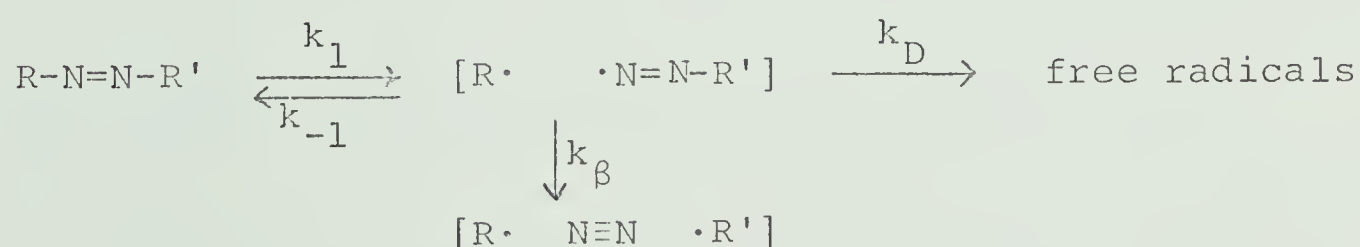
respectively. The kinetics for these compounds were measured in toluene solvent. Decomposition rates depend on steric effects as well as activation energies.

In an azo compound decomposition for which there is a possibility of giving either two or three fragments it

might be expected that the entropy of activation would be greater if three particles were produced. However, there are increased restrictions on the geometries of groups stabilizing incipient free radicals. If there is a one-bond scission, the alkyl group of the alkylazo radical contributes little to the stabilization and is therefore free to rotate, also increasing the entropy of activation. On the basis of activation parameters, nothing conclusive can be said about the decomposition mechanism of 4.

The decrease in the decomposition rate of 4 in changing the solvent from octane ($k = 4.28 \times 10^{-5}$) to hexadecane ($k = 3.95 \times 10^{-5}$) supports the argument that a two-step mechanism occurs. The difference in rate is 8% at 77.6°. Pryor (14) found a 15% difference in the rate of decomposition of p-nitrophenylazotriphenylmethane using octane and hexadecane as solvents at 77.5°.

The decomposition of an azo compound by a one-bond scission mechanism is represented below.



where k_1 = rate constant for bond homolysis

k_{-1} = rate constant for cage return

k_β = rate constant for β -scission of alkylazo radical

k_D = rate constant for diffusion

In solvents of such similarity as octane and hexadecane the rate constants k_1 , k_{-1} and k_β are expected to be the same in each solvent at a given temperature. In the more viscous solvent, k_D is decreased, thus enhancing cage return. The difference is manifested as an observed rate decrease in the decomposition of the azo compound. If the β -scission is very rapid compared to the rate of diffusion, there will be no viscosity dependence. In the case of 4, the positive viscosity test indicates that the lifetime of the 2-butylazo radical is at least of the same order of magnitude as the time required for diffusion of the initial radical pair. However, the β -scission of the 2-butylazo radical must be rapid inside the cage otherwise there would be greater net inversion in the unsymmetrical coupling product recovered from the decomposition of S-(-)-4, especially if the inversion mechanism is occurring by a radical displacement.

In summary, the experimental observations favouring a one-bond scission mechanism for the decomposition of 4 include a viscosity decomposition rate dependence, a small cage effect and net inversion of configuration in the recovered unsymmetrical coupling product. Although an explanation of the inversion observed requires initial one-bond scission, the details of the actual inversion process are not known.

E X P E R I M E N T A L

Physical measurements.

All melting points and boiling points are uncorrected. Melting points were taken on a Reichert Austria melting point apparatus. Infrared (i.r.) spectra were recorded on a Perkin-Elmer 421 Grating Spectrophotometer. Nuclear magnetic resonance (n.m.r.) spectra were obtained on a Varian Analytical Spectrometer, Model A-60, using tetramethylsilane (TMS) as internal reference. Solution optical rotations were measured with a Perkin-Elmer 141 Polarimeter and neat optical rotations were taken on a Rudolf Polarimeter, Model 80. Refractive indices (n_D) were taken on a Bausch and Lomb Abbe-3L Refractometer. Gas-liquid chromatography (g.l.c.) was carried out with an Aerograph 202 fractometer using a Honeywell recorder. For preparative work a 6 ft. $\times$ $\frac{1}{4}$ in. stainless steel tube packed with 20% SF-96 on Chromosorb P was used. For analytical work the column employed was a 10 in. $\times$ $\frac{1}{4}$ in. tube packed with 4% SF-96 on Chromosorb P. The carrier gas was helium.

Purification of solvents.

Benzene

Commercial benzene was shaken with successive portions of concentrated sulfuric acid until no decolourization of the acid occurred. It was then washed with three portions of saturated sodium bicarbonate and three portions of water.

After drying over magnesium sulfate the benzene was distilled from sodium metal through a Vigreux column. The middle fraction was collected and stored over molecular sieves.

Cumene

The same procedure as for benzene was employed. The middle cut of distillate was stored at 5° in the dark.

Octane

Practical grade octane was treated in the same manner as benzene.

Hexadecane

Practical grade hexadecane was extracted and washed in the usual manner then distilled at reduced pressure. The constant boiling fraction was stored at 5°.

1-Butanethiol

Commercial 1-butanethiol was distilled through a short Vigreux column. A middle cut of the distillate was collected and stored in a tightly stoppered bottle.

Neutralization of apparatus.

All pieces of apparatus with which compound 4 came in contact were carefully neutralized. After treatment overnight in a chromic acid bath the glassware was washed with distilled water then immersed in concentrated ammonia for

several hours. The ammonia was washed off with distilled water and finally the apparatus was baked out overnight at 130°. The stainless steel bomb was prepared similarly except that washing with ether and methanol replaced the treatment with chromic acid.

Solvent removal

Solvent removal was carried out at reduced pressure on a rotary evaporator unless otherwise stated.

Synthesis of diphenylmethylhydrazine, 1

To 50 g (1.56 mole) of anhydrous hydrazine in 150 ml of dimethylsulfoxide was added 30 g (0.4 mole) of sodium bicarbonate. With stirring, 70 g (0.35 mole) of freshly distilled diphenylmethylchloride in 50 ml of dimethylsulfoxide was added dropwise over a period of 20 minutes. The mixture was heated to 50° for two hours under a nitrogen atmosphere. The reaction mixture was then poured into ice water (200 ml) and the resulting solution extracted with methylene chloride (3 × 100 ml). The combined methylene chloride extracts were washed with water (2 × 100 ml), dried (MgSO₄), concentrated and distilled giving 55 g (80%) of the hydrazine 1, which crystallized to a white solid upon standing: m.p. 50-53° [lit. (4) m.p. 55-60°]; b.p. 122-124° (0.2 mm); n.m.r. (CCl₄), τ 2.78 (10.0H, m, aromatic), 4.50 (1.0H, s), 6.88 (3.0H, broad, -NH), required 10 : 1 : 3.

2-Butanone diphenylmethylhydrazone, 2

To 50 g (0.7 mole) of 2-butanone were added 23 g (0.12 mole) of diphenylmethylhydrazine and 20 g of anhydrous magnesium sulfate. The mixture was stirred under a nitrogen atmosphere at 50° for two hours then at room temperature overnight. The reaction mixture was filtered and the filtrate concentrated to remove excess 2-butanone. Distillation of the residue gave 16.8 g (60%) of a colourless oil, 2, which formed a white solid upon standing: b.p. 133-134° (0.15 mm); m.p. 33-35°; i.r. (CCl₄) 1610 (C=N); n.m.r. (CCl₄) τ 2.78 (9.9H, m, aromatic), 4.56 (1.0H, s), 5.31 (1.0H, broad, -NH), 7.95 (1.9H, q), 8.47 (2.95H, s), 9.06 (2.9H, t), required 10 : 1 : 1 : 2 : 3 : 3.

Analysis: Calculated for C₁₇H₂₀N₂: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.72; H, 8.02; N, 11.38.

1, 1-Diphenyl-1'-ethyl-1'-methylazomethane, 4

Method A

In a 100 ml round bottom flask, 1.5 g (0.006 mole) of hydrazone 2 was dissolved in 20 ml of methanol and 200 mg of platinum oxide catalyst was added. The mixture was treated with hydrogen at atmospheric pressure on a micro-hydrogenation apparatus. One equivalent of hydrogen was taken up within an hour. The catalyst was filtered and the solution concentrated. The residue was dissolved in 100 ml of ether and this solution was stirred in an

unstoppered flask for six hours. The etherial solution was dried (Na_2SO_4), concentrated and chromatographed on a column (1.5 cm $\times$ 25 cm) packed with 5 g of Florisil, 100-200 mesh. The azo compound was eluted in the first 50 ml of pentane eluant. Concentration of the eluant gave 0.38 g (25%) of 4, a pale yellow oil: n_D^{25} 1.5454; i.r. (neat) 1603 (N=N); n.m.r. (CCl_4) τ 2.77 (10.0H, m, aromatic), 4.48 (1.0H, s), 6.54 (0.95H, q), 8.35 (2.0H, m), 8.84 (3.1H, d), 9.26 (3.1H, t), required 10 : 1 : 1 : 2 : 3 : 3.

Analysis: Calculated for $\text{C}_{17}\text{H}_{20}\text{N}_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.76; H, 8.15; N, 11.13.

Method B

This reduction procedure was adapted from that described by Seltzer (10). A solution of 2.5 g (0.01 mole) of hydrazone 2 in 20 ml of ether was added dropwise over a period of one hour to a slurry of 0.51 g (0.013 mole) of lithium aluminum hydride in 100 ml of ether. The stirred mixture was kept under a nitrogen atmosphere while being refluxed for two days. Hydrolysis was carried out by adding dropwise successively 1 ml of water, 6 ml of 10% potassium hydroxide solution and 1 ml of water. After filtration the ether solution was stirred in an unstoppered flask for six hours then concentrated and the residue chromatographed as above, giving 0.5 g (20%) of

4 with the same n.m.r. spectrum as the previously synthesized compound.

Benzophenone hydrazone, 5

This compound was prepared as described previously (31). Benzophenone (97.3 g, 0.54 mole) in 200 ml of 1-butanol was treated with 50 g (1.3 mole) of 85% hydrazine hydrate and the mixture was heated under reflux for three hours. The product precipitated upon cooling and was recrystallized from ethanol yielding 73.5 g (70%) of 5, a white solid: m.p. 96-97° [lit.(32) m.p. 97-98°]; n.m.r. (CCl₄) τ 2.75 (10.4H, m, aromatic), 4.73 (2.0H, broad, -NH), required 10 : 2.

Diphenyldiazomethane, 6

Benzophenone hydrazone was treated with yellow mercuric oxide in a steel pressure bomb as previously described (32). The resulting diazo compound 6 was used immediately without purification.

Benzophenone 2-butylhydrazone, 7

Method A

A Grignard reagent was made in the usual manner from 30 g (0.33 mole) of 2-chlorobutane and 12 g (0.5 mole) of magnesium turnings, using 250 ml of ether as solvent. Beforehand, diphenyldiazomethane was prepared from 39.7 g

(0.2 mole) of benzophenone hydrazone and 44 g (0.2 mole) of yellow mercuric oxide. The Grignard reagent was cooled in an ice bath while a solution of the diazo compound in 75 ml of ether was added dropwise with stirring over 30 minutes. Upon completion of the addition, the mixture was allowed to stand at room temperature overnight; the red solution became nearly colourless and a yellow precipitate formed. The mixture was hydrolysed with ice and saturated aqueous ammonium chloride, the ether layer separated and the water layer extracted with ether (2 × 100 ml). The combined ether fractions were dried (CaCl_2), concentrated and distilled to give 36.4 g (72%) of the hydrazone 7, a viscous yellow oil which darkened rapidly upon exposure to air: b.p. $86-89^\circ$ (0.05 mm); n_D^{30} 1.5987; i.r. (neat) 1670 (C=N); n.m.r. (CCl_4) τ 2.75 (10.5H, m, aromatic), 5.05 (0.97H, broad, -NH), 6.75 (1.0H, m), 8.50 (2.1H, m), 8.87 (3.2H, d), 9.15 (3.0H, t), required 10 : 1 : 1 : 2 : 3 : 3.

Analysis: Calculated for $\text{C}_{17}\text{H}_{20}\text{N}_2$: C, 80.91; H, 7.99; N, 11.10. Found: C, 80.94; H, 8.12; N, 10.46.

1, 1-Diphenyl-1'-ethyl-1'-methylazomethane, 4

Method C

In a 300 ml three-necked flask fitted with an inlet tube and mechanical stirrer was placed 2.0 g (0.009 mole) of hydrazone 7 in 150 ml of ethylene glycol. A nitrogen

atmosphere was maintained in the vessel during the reaction. With vigorous stirring, 46 g (0.023 mole) of 4% sodium amalgam, prepared as described by Feiser (33), was added portionwise to the mixture over a period of 15 minutes. During this time, the reaction mixture was heated to 110° by means of an oil bath. A further 46 g of amalgam was added similarly after 30 minutes. After a total reaction time of 1.5 hours, the mixture was cooled and extracted with ether (3 × 100 ml). The combined ether extracts were washed with water (5 × 100 ml) and dried (Na_2SO_4). Oxidation of the resulting intermediate hydrazo compound 3 was carried out as before. Column chromatography yielded 0.3 g (15%) of azo compound 4, identical to that described previously.

Resolution of 2-butylamine

This was carried out by a modification of the method of Fleury-Larsonneau (45). To 48 g (0.66 mole) of 2-butylamine in 25 ml of water was added with stirring and cooling 40% aqueous d-tartaric acid until the solution was neutral to litmus. An equal volume of the acid solution was added in one portion to form the bitartrate salt. The aqueous solution was concentrated to 265 g then allowed to stand overnight at 10°. The solid mass of crystals which formed was filtered and dried then recrystallized from water using 1.2 g of solvent per gram of salt.

The recrystallization was carried out for one day at room temperature then for a further three days at 10°. The crystals were recovered and the recrystallization procedure repeated using 1 g of water per gram of salt. The yield of twice re-crystallized salt was 30 g.

The resolution was carried out on a large scale using 2000 g of amine in 50 g portions, treated as above. The yield of salt was 1200 g. To recover the amine, the salt was dissolved in a minimum amount of water and hydrolysed by the addition of excess sodium hydroxide. Distillation at atmospheric pressure afforded a mixture of amine and water. Sodium hydroxide pellets were added to the mixture until no more water was extracted into the lower phase. The organic layer was refluxed over solid sodium hydroxide for one hour then distilled. The operation was repeated on the distillate giving 220 g of (S)-(+)-2-butylamine: n_D^{25} 1.3925 [lit. (60) n_D^{25} 1.3930]; $[\alpha]_D^{25}$ + 7.21 (l, 1 dm, neat). This represents an optical purity of 92% (61). The n.m.r. spectrum was the same as that of an authentic sample.

N-2-Butylsydnone, 10

The method used is similar to the general method of Hunsberger (38). A solution consisting of 200 g (2.74 mole) of 2-butylamine in 700 ml of sodium-dried benzene was placed in a 2000 ml round-bottom flask fitted with a reflux condenser, drying tube and magnetic stirrer. Ethyl

chloroacetate (166 g, 1.36 mole) was slowly added to the stirred solution and the resulting mixture was heated under reflux for 6.5 hours, then cooled. A white precipitate of 2-butylamine hydrochloride was filtered off and the filter cake washed with benzene. The combined filtrate was concentrated and the residual crude N-2-butylglycine acetate, 8, was saponified by adding it over a period of 30 minutes to a gently boiling solution of 60 g (1.5 mole) of sodium hydroxide in 300 ml of water. After the addition was complete, the mixture was heated under reflux for a further 45 minutes, then cooled to room temperature. The reaction mixture was extracted with ether (3 × 200 ml) and the ether extracts discarded. A solution of 110 g (1.6 mole) of sodium nitrite in 150 ml of water was added to the aqueous phase and the resulting mixture cooled by means of a dry ice-acetone bath to -5°. With vigorous stirring, 240 ml of concentrated hydrochloric acid was added dropwise over a period of one hour, during which time the temperature was maintained between 0° and -10°. The reaction mixture was extracted with ether (3 × 200 ml) and the combined ether extracts washed with water (2 × 200 ml) and concentrated to give a yellow solid, N-nitroso-N-2-butylglycine, 9.

Without purification, compound 9 was treated with 450 g (4.4 mole) of acetic anhydride and the mixture was

heated on a steam bath for four hours, then left at room temperature for one day. The acetic anhydride was removed by distillation at 30 mm, leaving a dark brown viscous oil which was distilled under high vacuum to yield 66.5 g (35%, based on 2-butylamine) of N-2-butylsydnone, 10, a viscous yellow oil: b.p. 107° (0.05 mm) lit. (37) b.p. 130° (0.3 mm) ; i.r. (neat) 1760 (C=O), 3140 (C-H, aromatic); n.m.r. (CCl₄) τ 3.34 (1.05H, s), 5.48 (1.0H, sextet), 8.07 (2.05H, q), 8.37 (3.1H, d), 9.03 (3.1H, t), required 1 : 1 : 2 : 3 : 3.

S-(+)-N-2-Butylsydnone, (+)-10

This compound was synthesized from (S)-(+)-2-butylamine as described above: $[\alpha]_D^{25}$ 48.8° (c 11.5, CCl₄). The n.m.r. spectrum was essentially the same as that of the racemic compound.

2-Butylhydrazine, 11

Method A

The sydnone 10 was hydrolysed by a method adapted from one previously described (30). Concentrated hydrochloric acid (150 ml, 1.8 mole) was mixed with 50 g (0.35 mole) of 10 and the mixture heated on a steam bath for 2.5 hours. Carbon dioxide evolution was rapid at first then gradually decreased until no bubbling was detected. The mixture was cooled in an ice bath and 320 g (2.0 mole) of 25% aqueous

sodium hydroxide was added over a period of 30 minutes. The mixture was distilled at atmospheric pressure under nitrogen, 150 ml of distillate being collected. Potassium hydroxide pellets were added to the distillate, resulting in the formation of two phases. The upper organic layer was separated and distilled under nitrogen from anhydrous barium oxide, yielding 20.2 g (65%) of colourless 2-butylhydrazine, 11: b.p. 102-105° (700 mm); n_D^{25} 1.4024; i.r. (neat) 3350 (broad, -NH); n.m.r. (CCl₄) τ 6.47 (3.10H, broad, -NH), 7.46 (0.95H, m), 8.30-9.30 (8.0H, complex pattern from one methylene and two methyl groups), required 3 : 1 : 8. The compound has been reported previously (62) but no physical constants were given except the m.p. of the hydrochloride salt.

S-(-)-2-Butylhydrazine, (-)-11

The preparation was carried out as above, giving hydrazine with essentially the same n.m.r. spectrum as the racemic material. The optical rotation obtained was $\alpha_D^{25} = -3.35^\circ$ (1 dm., neat).

Benzophenone 2-butylhydrazone, 7

Method B

In a 100 ml three-necked flask fitted with a drying tube, reflux condenser and inlet tube, 6.0 g (0.033 mole) of benzophenone was dissolved in 15 ml of 1-butanol. To this was added in one portion 8.0 g (0.09 mole) of

2-butylhydrazine and the reaction mixture was refluxed for 24 hours under a nitrogen atmosphere. The mixture was concentrated and the residue distilled, giving 2.5 g (30%) of the hydrazone 7, identical to that obtained by treatment of 2-butylmagnesium chloride with diphenyl-diazomethane described previously.

S-(-)-1,1-Diphenyl-1'-ethyl-1'-methylazomethane, (-)-4

Benzophenone 2-butylhydrazone was prepared as above from S-(-)-2-butylhydrazine of 92% optical purity. The optically active azo compound was prepared from the hydrazone in the manner reported previously. It was shown to be pure by its n.m.r. spectrum. The optical rotation obtained was $[\alpha]_D^{25} = -2.8^\circ$ (c 2.93, CCl_4).

Resolution of 2-methylbutanoic acid

The resolution was accomplished by the method of Odham (44). Initially, the resolving agent, α -phenylethylamine was in turn resolved by the method of Thielacker (43) but later it was obtained commercially.

To 30.8 g (0.3 mole) of freshly distilled 2-methylbutanoic acid in 150 ml of ether-petroleum ether (1:1 mixture by volume) was added dropwise with cooling a solution of 22.5 g (0.19 mole) of (-)- α -phenylethylamine, $[\alpha]_D^{20} = -40.2^\circ$, in 150 ml of the same mixed solvent. Crystallization was allowed to take place overnight at -20° . This same procedure was carried out with 12 separate

samples. The combined solid obtained was dissolved in a minimum volume of ether-petroleum ether (3:1 mixture, by volume) and allowed to stand at room temperature for two hours then left at 10° overnight. This recrystallization procedure was repeated five more times, giving 57 g of the salt. The salt was hydrolysed with 10% aqueous sodium hydroxide and the mixture extracted with ether (3 × 50 ml) to remove the optically active amine. The aqueous phase was acidified with 3N hydrochloric acid and the solution extracted with chloroform (3 × 50 ml). The combined chloroform extracts were washed with water (2 × 50 ml), concentrated and distilled to give 23.4 g of (-)-2-methylbutanoic acid: b.p. 75-76° (23 mm) lit. b.p. (44) 67-68° (12 mm) ; $[\alpha]_D^{24} -16.4^\circ$ (l, 1 dm, neat). This rotation represents an optical purity of 85% (44).

2-Methylbutyrylchloride, 12

The procedure was based on that given for the preparation of 2-methylpropionylchloride (63). With rapid stirring, 48 g (0.47 mole) of 2-methylbutanoic acid was added over a period of 10 minutes to 60 g (0.5 mole) of thionyl chloride. The mixture was heated to 70° for 40 minutes at which point gas evolution had practically ceased. The mixture was distilled to give 36.5 g (65%) of the acid chloride 12: b.p. 109° (695 mm) [lit, (64) b.p. 119-120° (760 mm)]; n.m.r. (CCl_4) τ 7.22 (1.0H, sextet), 8.33

(2.0H, m), 8.71 (2.9H, d), 9.00 (2.9H, t), required 1 : 2 : 3 : 3.

1,1-Diphenyl-2-methyl-1-butanol, 13

Method A

The compound was obtained by the procedure of Huston (39), exactly as described. From 36 g (0.3 mole) of acid chloride 12 there was prepared 43 g (60%) of alcohol 13: b.p. 113-114° (0.3 mm) [lit. (39) b.p. 126° (1.0 mm)]; n_D^{25} 1.5630; i.r. (neat) 3580 (-OH); n.m.r. (CCl₄) τ 2.72 (9.8H, m, aromatic), 7.60 (1.0H, m), 8.07 (1.05H, s, -OH), 8.40-9.30 (7.8H, complex pattern from one methylene and two methyl groups), required 10 : 1 : 1 : 8.

Method B

The same procedure was used as described above except that the ethyl ester of 2-methylbutanoic acid was used in place of the acid chloride 12. The alcohol 13 was obtained in only 15% yield and contained undetermined impurities as shown by its n.m.r. spectrum. The reaction was not investigated further.

R-(-)-1,1-Diphenyl-2-methyl-1-butanol, (-)-13

This was synthesized by the acid chloride route described above from (-)-2-methylbutanoic acid which was 85% optically pure. The product, whose n.m.r. spectrum was the same as the racemic material had a m.p. of 33-38°

and rotation $[\alpha]_D^{25} = -20.2$ (c 9.3, CCl_4).

1,1-Diphenyl-2-methylbutane, 14

The procedure used was a modification of the technique developed by Birch (41) for hydrogenolysing benzylic alcohols. A 500 ml three-necked flask fitted with a magnetic stirrer and an air condenser filled with dry ice-acetone was cooled in a dry ice-acetone bath. Into this was run 150 ml of liquid ammonia. The alcohol 13 (7.0 g, 0.03 mole) together with 3.0 g (0.05 mole) of ethanol was dissolved in the ammonia. Over a period of 10 minutes 1.5 g (0.07 mole) of sodium metal was added in small pieces. The solution became dark blue and then colourless again after a few minutes. After the cooled solution had been stirred for 30 minutes, it was left for the ammonia to evaporate overnight. Water was added to the solid residue and the mixture extracted with ether (2×50 ml). The combined ether extracts were washed with water (3×50 ml), dried (MgSO_4), concentrated and distilled to give 5.8 g (89%) of the hydrocarbon 14: b.p. $86-87^\circ$ (0.15 mm); n_D^{25} 1.5501; n.m.r. (CCl_4) τ 2.82 (10.0H, m, aromatic), 6.50 (1.0H, d), 7.80 (1.0H, m), 8.50-9.30 (8.0H, complex pattern from one methylene and two methyl groups), required 10 : 1 : 1 : 8.

Analysis: Calculated for $\text{C}_{17}\text{H}_{20}$: C, 91.01; H, 8.99.
Found: C, 91.29; H, 8.99.

R-(-)-1,1-Diphenyl-2-methylbutane, (-)-14

The optically active hydrocarbon was synthesized by the above method from (-)-13 of 85% optical purity. The n.m.r. spectrum of the product was the same as for the racemic compound. The rotations obtained were $[\alpha]_D^{25} = -12.8^\circ$ (1 dm., neat) and $[\alpha]_D^{25} = -13.8^\circ$ (c 9.43, CCl_4).

1,1,2,2-Tetraphenylethane, 15

In a three-necked round bottom flask fitted with a dropping funnel, reflux condenser and drying tube were placed 1 g (0.04 mole) of magnesium turnings and 125 ml of ether. To this, 10 g (0.05 mole) of diphenylmethylchloride dissolved in 50 ml of ether was added with stirring over a period of 10 minutes. During the addition a white precipitate began to form. The reaction mixture was stirred for two hours then the crude product was isolated by filtration. Two recrystallizations from ethanol afforded 3.5 g (43%) of hydrocarbon 15, as white needles: m.p. 210° [lit. (42) m.p. 211°]; n.m.r. (CDCl_3) τ 2.95 (10.0H, m, aromatic), 5.24 (1.0H, s), required 10 : 1.

2-Butylhydrazine, 11Method B

This procedure was adapted from the general method of Smith (30) for obtaining alkyl hydrazines. To a mixture of 28 g (0.11 mole) of benzophenone 2-butylhydrazone, 7 and 60 ml of absolute ethanol was added with swirling 40 ml

(0.48 mole) of concentrated hydrochloric acid. The reaction vessel was flushed with nitrogen, stoppered and left overnight at room temperature. The mixture was then concentrated and the residue washed with ether (2×50 ml). The aqueous solution was hydrolysed by the addition of 80 g (0.48 mole) of 25% aqueous sodium hydroxide and this mixture was distilled under a nitrogen atmosphere to give a solution of hydrazine and water. The hydrazine was isolated as described previously resulting in 6.4 g (65%) of 11 whose n.m.r. spectrum was the same as that of the material prepared via the sydnone route.

Alternate method for oxidation of 3

The recently invented reagent of silver carbonate on celite support was prepared as reported (65). The hydrazone 2 (1.4 g, 0.006 mole) was reduced to the hydrazo compound 3 by catalytic reduction in the usual manner. After filtration of the catalyst, the methanolic solution was concentrated and the residue dissolved in 35 ml of ether. With stirring, 4 g (0.007 mole) of silver carbonate on celite was added. The suspension gradually darkened and was black after 15 minutes. The mixture was stirred a total of 30 minutes then filtered and the filtrate concentrated then chromatographed as before. There was obtained 0.31 g (22%) of azo compound 4, identified by its n.m.r. spectrum.

Decomposition kinetics of 4

The kinetics were followed by monitoring the nitrogen evolution during the decomposition of 4.

The decompositions were carried out in a tube of capacity 3 ml which was attached to a 24/40 tapered joint. For runs using dilute solutions, a reaction vessel of capacity 10 ml was employed. A rubber serum cap covered the open end of the reaction vessel which was attached by means of capillary tubing to a water-jacketed gas burette. A capillary side-arm which could be closed off was used for flushing the system. The decomposing solution was maintained at a constant temperature by immersing it in the refluxing vapours of a solvent held in a three-necked flask. The three-necked flask was fitted with a glass stopper in one neck and a reflux condenser in another. The reaction vessel was placed in the third neck. A glas-col heating mantle was used to heat the flask, care being taken not to superheat the vapour. The temperature of the vapour was measured with a thermometer and a stem correction was applied to the reading. Alternatively, the temperature could be inferred by the ambient pressure.

In a typical run, freshly prepared azo compound 4 (0.28 g) was dissolved in 2.1 ml of purified cumene and the solution placed in the reaction vessel. Nitrogen was

bubbled through the solution for 10 minutes to minimize the amount of oxygen present. The serum cap was put in place and the apparatus flushed with nitrogen. The system was closed off and the vessel inserted in the middle neck of the three-necked flask, thus immersing the reaction tube in the vapours of the refluxing solvent. It took approximately six minutes to establish equilibrium in the system. Readings of the gas burette were taken every two or three minutes for 30 minutes then every four or five minutes for another hour. After four hours (about 10 half-lives) the nitrogen evolution had ceased and the burette reading was constant. A final volume reading, V_{∞} , was recorded.

From the slope of the graphical plot of $\log (V_{\infty} - V_t)$ versus t the unimolecular rate constant was calculated as shown in Table I and Figure I. A summary of all the results obtained is given in Table III.

Product Analysis

Decompositions of 4 were carried out in evacuated sealed tubes which were made from cylindrical glass tubing of diameter 9 mm. The tubing was cut into 20 cm lengths, sealed at one end then neutralized in the usual manner.

The azo compound used in these experiments was synthesized via Scheme I. Generally, 0.5 ml of a 0.2 M solution of 4 in benzene or 1 M butanethiol in benzene was

placed in a reaction tube which was then connected to the high vacuum rack. The solution was de-gassed by a series of three freeze-thaw cycles. A vacuum of 25 μ could be attained over the frozen solution. The tube was sealed off under vacuum, the sealed tube being about 10 cm in length. In this manner a series of tubes were prepared so that they could later be heated simultaneously. Duplicate samples were made up for each set of reaction conditions.

The tubes were placed in a pre-heated oven maintained at either $100 \pm 1^\circ$ or $80 \pm 1^\circ$ and left for at least 10 half-lives. They were removed, cooled to -70° and opened. The contents were transferred to stoppered vials.

Product analysis of unscavenged decompositions

The decomposed solutions were analysed on the Aerograph 202 fractometer. Previously, solutions of known composition containing the compounds diphenylmethane, 14 and 15 were analysed to determine appropriate molar response factors. The factors were calculated in such a way that the areas of the peaks of the chromatograms were multiplied by their appropriate response factors to give the relative molar composition of the mixture. The factors were as follows: diphenylmethane, 1.61; 14, 1.37 and 15, 1.00. Unidentified compounds assumed to contain a diphenylmethyl fragment were arbitrarily assigned a response factor of 1.00.

Response factor calibration and product analyses were carried out on the same day so that any lack of reproducibility which was instrumental in origin would be minimized.

The injector temperature was set at 240° and the detector at 280° . With the column temperature at 80°, a 5 µl injection of the decomposition solution was made then the temperature was increased manually to 220° over 15 minutes. The gas flow was 60 ml per minute measured at 80°.

Two good chromatograms were obtained for each sample. In order to determine the relative peak areas, the peaks were carefully cut out of the chromatograms and weighed on an analytical balance. The results are summarized in Table IV.

Product analysis of scavenged decompositions

The analyses were carried out using the same conditions as for the unscavenged runs. The effluent stream from the collection port of the gas chromatograph was carried away by a vacuum line to prevent contamination of the room's atmosphere by butanethiol. The results obtained are given in Table V.

Decompositions of S-(-)-4

These decompositions were carried out in a carefully

neutralized 75 ml stainless steel pressure bomb. The azo compound (0.7 g) was dissolved in 20 ml of benzene and the solution was placed in the bomb. The solution was flushed with nitrogen and the reaction vessel stoppered then placed in a preheated oven maintained at 100° and left overnight, about 15 half-lives.

The bomb was cooled, opened and the contents concentrated by distillation at atmospheric pressure. The residue was injected in 10 μ l portions into the gas chromatograph and the product of interest R-(-)-14, was collected in the effluent stream.

The injector and detector temperatures were 220° and 280° respectively. From an initial temperature of 100°, the column temperature was increased manually at approximately 5° per minute until the desired compound was eluted, near 150°. The temperature was then increased rapidly to 225° and left until all of the compounds with longer retention times than 14 had been eluted.

The butanethiol scavenged run was carried out similarly. The results are summarized in Table VI.

CIDNP experiments on 4

A quantity of 4 was synthesized via Scheme I. Portions of the azo compound (0.5 g) were placed in sample vials and an equal number of sample vials containing 0.5 ml of purified hexadecane was placed in a

preheated oven maintained at 120°. A portion of 4 was transferred to an n.m.r. sample tube, followed by an aliquot of hot hexadecane. A wad of cotton was inserted in the top of the tube to prevent the liquid from being carried out by the nitrogen evolution. The tube was shaken then placed in the n.m.r. probe at 120°. The spectrum was scanned from τ_2 to τ_8 as long as the effect could be observed, generally about six minutes.

Preheating of the solvent decreased the amount of time required to reach thermal equilibrium in the probe. Very little nitrogen evolution occurred in the time elapsed between mixing the solvent and azo compound and placing the sample in the probe.

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